Tetrahedron, 1963, Vol. 19, pp. 1415 to 1421. Pergamon Press Ltd. Printed in Northern Ireland

MEXICANIN—I. A NEW SESQUITERPENE LACTONE RELATED TO TENULIN

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(*Received* 14 *February; revised form* 29 *March*)

Contribution No. 151 from the Instituto de Química de la Universidad Nacional Autónoma de México.

Abstract—Mexicanin I a new sesquiterpene lactone isolated from *Helenium mexicanum* H.B.K. has been correlated with tenulin.

THE isolation of helenalin from *Helenium mexicanum* H.B.K., collected near Nochistlán (Estado de Oaxaca), has been recently reported.[1] We have now isolated in small amount another component from the extract of the plant, which we propose to name mexicanin I. This product belongs to the group of C_{15}-lactones obtained from *Helenium mexicanum*.[2,3] From this plant there have been isolated three series of lactones; the C_{14} group which includes mexicanins E[1] and F[2]; the C_{15}-group with helenalin and mexicanins A[4], C[3], D[3] and H[2]; to the C_{17}-group belong mexicanins B[3] and G[2].

Mexicanin I is a cystalline substance ($C_{15}H_{18}O_4$) m.p. 257–260°, $[\alpha]_D$ +42·5°, its I.R. spectrum indicates that the four oxygen atoms are distributed as a secondary hydroxyl group (band at 3560 cm^{-1}, formation of an acetate, oxydation to a ketone), an unsaturated γ-lactone (bands at 1768 and 1668 cm^{-1}) and a cyclopentenone (bands at 1707 and 1585 cm^{-1}). Mexicanin I has two double bonds involved in two different chromophores: an exocyclic methylene group and a cyclopentenone, as shown by the following evidence: The U.V. absorption spectrum of mexicanin I (λ_{max}, 216 mμ; ε, 14,420) is very similar to those of helenalin and ambrosin.[5–7] It forms a dipyrazoline on treatment with diazomethane. The N.M.R. spectrum† of mexicanin I acetate (Ib)

* Taken in part from a Thesis to be submitted by E. Domínguez to the Universidad Nacional Autónoma de México in partial fulfilment of the requirements to obtain the degree of Doctor en Ciencias Químicas.

† The N.M.R. spectra were run on a Varian A-60 spectrophotometer, in chloroform solution, using tetramethylsilane as internal standard. We are indebted to Dr. Fernando Walls for his assistance.

[1] A. Romo de Vivar and J. Romo, *J. Amer. Chem. Soc.* **83**, 2326 (1961).
[2] A. Romo de Vivar and J. Romo, *Ciencia*, Mex. **21** (1), 33 (1961).
[3] A. Romo de Vivar and J. Romo, *Chem. & Ind.* 882 (1959).
[4] W. Herz, A. Romo de Vivar, J. Romo and N. Viswanathan, *J. Amer. Chem. Soc.* **85**, 19 (1963).
[5] R. Adams and Herz, *J. Amer. Chem. Soc.* **71**, 2546 (1949).
[6] H. Abu-Shadi and T. O. Soine, *J. Amer. Pharm. Assn.* **42**, 387 (1953).
[7] L. Bernardi and G. Büchi, *Experientia* **13**, 466 (1957).

displays in the vinyl proton region two low field doublets (intensity one proton each), centered at 6·23 and 5·65 p.p.m., ascribed to the exocyclic methylene group (J = 3·4 c.p.s.), and two sets of quadruplets (intensity one proton each), centered at 7·63 and 6·08 p.p.m. corresponding to the A and B protons of an ABX spectrum associated with the cyclopentenone chromophore, ($J_{AB} = 6$, $J_{AX} = 3$, $J_{BX} = 3$), a doublet at 5·92 p.p.m. (intensity one proton), corresponding to the proton on the carbon bearing the acetoxy group, (J = 4·8 c.p.s.). Three pairs of doublets, centered at 4·8 p.p.m., associated with the proton at C_8 (lactonic ring closure). In the methyl region it had a sharp signal at 2·07 p.p.m. (intensity three protons), corresponding to the acetoxy group and a doublet at 1·28 p.p.m. (intensity six protons).

The U.V. maximum of mexicanin I undergoes a bathochromic shift, when its hydroxyl group is oxydized to a ketone (II). The new maximum (λ_{max}; 230 mμ; ε, 14,800) is a composite of two chromophores, the cyclopentenone and the unsaturated lactone, in which the double bond has migrated to endocyclic conjugation with the new ketone. We could confirm this assumption since the N.M.R. spectrum exhibited only two vinyl protons, corresponding to the cyclopentenone, two quadruplets centered at 7·70 and 6·14 p.p.m. In the methyl region it showed a slightly split singlet at 2·22 p.p.m. (intensity three protons), associated with a vinylic methyl group (J = 2·5 c.p.s.). A sharp signal at 1·46 p.p.m. corresponding to a tertiary methyl group and a doublet at 1·31 p.p.m. ($\diagdown$ CH $-CH_3$), (J = 6·2 c.p.s.). The I.R. spectrum of dehydroisomexicanin I (II) had a broad band with three peaks: at 1755 (γ-lactone), at 1725 (displaced cyclopentenone), and at 1685 cm^{-1} (cycloheptenone), and two weak bands at 1628 and 1600 cm^{-1} (C—C double bonds).

Chemical reduction of dehydroisomexicanin I (II) with zinc in acetic acid, saturated both double bonds, yielding dehydrotetrahydromexicanin I (V). Its I.R. spectrum had a broad band at 1755 cm^{-1} (γ-lactone and cyclopentanone) and a relatively weak band at 1706 (cycloheptanone). Catalytic hydrogenation of mexicanin I afforded a dihydroderivative (III). The double bond that underwent hydrogenation was that of the cyclopentenone, since a new I.R. band at 1740 cm^{-1} corresponds to a cyclopentanone. The rotary dispersion curve* of the dihydrolactone (III) has a positive Cotton effect, while that of mexicanin I is negative. These results are in accord with the Cotton effects exhibited respectively by dihydroisotenulin and tenulin.[8] Suggesting the same five membered ring chromophores and identical stereochemical environment in the cyclopentane moiety. The remaining double bond of the dihydroderivative (III) is in endocyclic conjugation with the lactone (I.R. bands at 1770 and 1610 cm^{-1}), (λ_{max} 222 mμ; ε, 7000) and resisted hydrogenation. This entocyclic shift often takes place on hydrogenation of unsaturated lactones.[9,4]

The N.M.R. spectrum did not register signals corresponding to vinyl protons. In the methyl region is displayed a slightly split singlet at 1·95 p.p.m. (intensity three protons) ($\diagdown\!\!\diagdown$ C—CH_3), (J = 1 c.p.s.) a characteristic sharp signal at 1·13 p.p.m.

* We are indebted to Syntex, S.A. for the determination of the O.R.D. curves.

[8] C. Djerassi, J. Osiecki and W. Herz, *J. Org. Chem.* **22**, 1361 (1957).

[9] W. Herz, H. Watanabe, M. Miyasaki and Y. Kishida, *J. Amer. Chem. Soc.* **84**, 2601 (1962).

(—C —CH_3) and a doublet at 1·07 p.p.m. (intensity three protons), (J = 4·5 c.p.s.), (CH —CH_3). The salient features of the N.M.R. spectra of the mexicanin I derivatives described above, particularly the sharp signal due to a tertiary methyl group, strikingly resemble those of parthenin,[9] tenulin,[10] and helenalin,[4] which possess an abnormal guaianolide nucleus.

Chromium trioxide oxydation of dihydroisomexicanin I (III) afforded a diketone (IV). The I.R. spectrum had bands at 1760 (γ-lactone and cyclopentanone), at 1690 (cycloheptenone) and a weak band at 1635 cm^{-1} (C—C double bond). The U.V. maximum (λ_{max} 243 mμ; ε, 10,736), corresponds to that of a ketone conjugated with the lactonic chromophore. Reduction of dehydrodihydroisomexicanin I (IV) with zinc in acetic acid yielded a saturated diketone (V), which proved to be identical with that obtained in a similar manner from dehydromexicanin I (II), (*vide supra*). Mexicanin I was correlated with tenulin (IX), when the diketone (V) was identified with dehydrodesacetyldihydroisotenulin.[11,12] Therefore, mexicanin I is an "abnormal" guaianolide, with the same asymmetrical centers at C_1, C_5, C_8 and C_{10} and identical lactone closure at C_8. The centers at C_6 and C_7 have also the same configuration as in tenulin, since desulfuration of the adduct of mexicanin I with benzylmercaptan yielded tetrahydromexicanin I (VIa), which proved to be identical with desacetyldihydroisotenulin.[11,12] Herz* and Mitra[13] have correlated the tenulin and helenalin series; they have found that the two series differ at the C_6 and C_8 asymmetrical centers. Therefore mexicanin I differs from helenalin at C_6 and C_8 also, though both lactones posess the same structural formula.

Acetylation of tetrahydromexicanin I (VIa), afforded an acetate (VIb) (dihydroisotenulin[11,12]). This derivative is very probably epimeric at C_{11} with a product obtained by catalytic hydrogenation of mexicanin I acetate (Ib).

Mexicanin I undergoes a rearrangement in alkaline medium giving rise to products of the "neo" type, like those produced in the alkaline treatment of helenalin and tenulin.[11,12,14]

The U.V. spectrum of mexicanin I in alkaline medium developed a different maximum (λ_{max}, 236–238 mμ; ε, 10800). Mild treatment of the lactone with methanolic potassium bicarbonate yielded two products (a) and (b). The derivative (a) (VIIa), m.p. 259–263°, analyzed for $C_{15}H_{18}O_4$. Its U.V. spectrum (λ_{max} 210, 239 mμ; ε, 9,900, 15,000) indicates the presence of the exocyclic methylene group conjugated with the lactone and a new cyclopentenone chromophore. This assumption is confirmed by the I.R. spectrum, which exhibited the following bands: at 3330 (secondary

* We are grateful to Dr. Werner Herz who kindly carried out the comparison of our products with authentic specimens.

[10] W. Herz, W. A. Rohde, K. Rabindran, P. Jayataman and W. Viswanathan, *J. Amer. Chem. Soc.* **84,** 3857 (1962).

[11] B. H. Braun, W. Herz, and K. Rabindran *J. Amer. Chem. Soc.* **78,** 4423 (1956).

[12] D. H. R. Barton and P. de Mayo, *J. Chem. Soc.* 142 (1956).

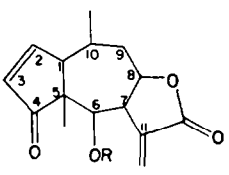
[13] W. Herz and R. B. Mitra, *J. Amer. Chem. Soc.* **80,** 4876 (1958).

[14] W. Herz, P. Jayaraman and H. Watanabe, *J. Amer. Chem. Soc.* **82,** 2276 (1960).

hydroxyl group, formation of an acetate) 1770 (γ-lactone), 1698 (cyclopentenone) and 1635 cm^{-1} (C—C double bond). The N.M.R. spectrum of the acetate (VIIb) possesses similar features as those reported for neohelenalin[4] and neotenulin.[10]

Derivative (b), m.p. 168–170°, is a methoxy-dihydroneomexicanin I (VIII), in which methanol addition took place at the exocyclic methylene group. Since it analyzed for $C_{16}H_{22}O_5$. The U.V. spectrum (λ_{max}, 240 mμ; ε, 12,900) and the I.R. bands at 3330 (hydroxyl group), 1770 (γ-lactone), 1690 (cyclopentenone) and 1630 cm^{-1} (C—C double bond), are in accord for the "neo" formulation, which is fully substantiated by the N.M.R. spectrum. It displayed no signals in the vinyl proton region. It had two sharp signals (intensity 3 protons each), at 3·33 p.p.m., associated with the methoxy group, and at 1·70 p.p.m. corresponding to the vinylic methyl group. A doublet at 1·14 p.p.m. (intensity three protons) (J = 6·8 c.p.s.), indicates the presence of a methyl on a secondary carbon atom. This type of addition has been reported to occur in costunolide.[15]

When the alkaline treatment of mexicanin I was carried out in t-butyl alcohol, only neomexicanin I (VIIa) was isolated.



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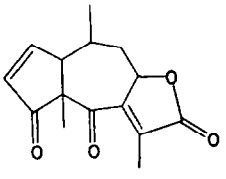

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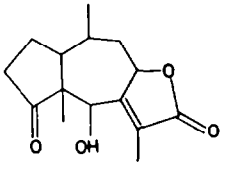

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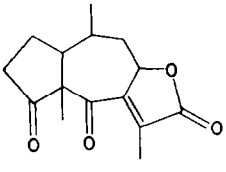

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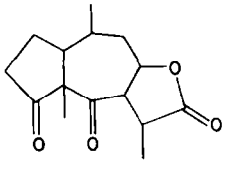
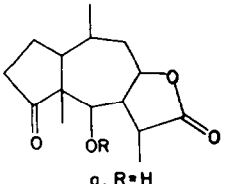


V



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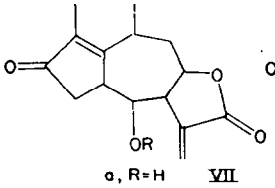
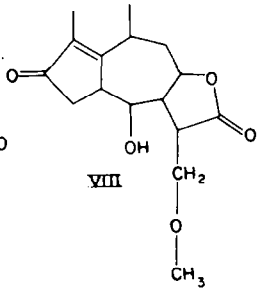
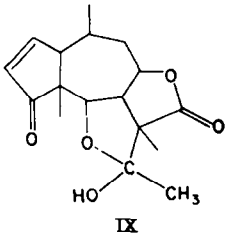


VII



VIII



IX

[15] G.H. Kulkarni, A. Paul, A. Somasekar Rao, G. R. Kelkar and S. C. Bhattacharya, *Tetrahedron* **12**, 178 (1961).

EXPERIMENTAL*

Isolation of mexicanin I. After the isolation of helenalin from *Helenium mexicanum* (collected near Nochistlán, Estado de Oaxaca)[1], its mother liquors crystallized from benzene, yielding mexicanin I (Ia, 430 mg) m.p. 246–253°. Several crystallizations from chloroform–methanol afforded prisms, m.p. 257–260°, $[\alpha]_D$ +42·5°; λ_{max} 216, 318–324 mμ; ε, 14420, 47); (in alkaline medium, λ_{max}, 236–238 mμ; ε, 10800); ν_{max} 3560, 1768, 1668, 1707 and 1585 cm^{-1}. Rotatory dispersion (in dioxane) $[\alpha]_{700}$ +46°, $[\alpha]_{589}$ +46°, $[\alpha]_{375}$ −522·2°, $[\alpha]_{367\cdot5}$ −574·6°, $[\alpha]_{350}$ −309·5°. (Found: C, 68·54; H, 6·96; O, 24·49; Calc. for $C_{15}H_{18}O_4$: C, 68·68; H, 6·92; O, 24·40%).

Mexicanin I *acetate* (Ib). Mexicanin I (Ia; 150 mg) was dissolved in acetic anhydride (2 ml) and pyridine (2 ml). The solution was heated for 1 hr on the steambath, diluted then with water and the precipitate collected. The acetate (Ib) crystallized from acetone–ether, yielding prismatic needles (130 mg), m.p. 200–203°; $[\alpha]_D$ +26·5°; λ_{max} 215 mμ; ε, 14650; ν_{max}; 1755, 1710 and 1590 cm^{-1}. Rotatory dispersion (in dioxane) $[\alpha]_{700}$ + 50·9°, $[\alpha]_{589}$ + 36·3, $[\alpha]_{375}$ −680°, $[\alpha]_{370}$ −718°, $[\alpha]_{365}$ −685·45°. (Found: C, 66·96; H, 6·45; O, 26·43; Calc. for $C_{17}H_{20}O_5$: C, 67·09; H, 6·62; O, 26·29%).

Mexicanin I *dipyrazoline*. Mexicanin I (Ia; 150 mg) was dissolved in methanol (20 ml) and mixed with an ethereal solution of diazomethane (prepared with 2 g of N-nitrosomethylurea.) The dipyrazoline began to crystallize in a few minutes. The solution was left at room temp for 30 min. The excess of diazomethane was destroyed by adding a few drops of acetic acid and the crystals collected and washed with ether, m.p. 182–185° dec. (90 mg). The analytical sample showed m.p. 185° dec. (small needles from methanol–ether). λ_{max}, 214, 322 mμ; ε, 2520, 190. (Found: C, 58·99; N, 6·26; O, 19·15; N, 15·93; Calc. for $C_{17}H_{22}O_4N_4$: C, 58·94; H, 6·40; O, 18·48; N, 16·18%).

Dehydroisomexicanin I (II). A solution of mexicanin I (Ia; 200 mg) in acetic acid (8 ml) was treated with 150 mg chromium trioxide dissolved in 1 ml water and 4 ml acetic acid, the mixture was left at room temp for 1 hr, diluted with water and extracted with chloroform. The extract was washed with water, 5% sodium carbonate solution and water again. The solution was evaporated to dryness and the solid residue crystallized from acetone–ether, yielding needles (90 mg), m.p. 198–202°. Several crystallizations from acetone–methanol raised the m.p. to 232–235°; $[\alpha]_D$ +129°; λ_{max} 230 mμ; ε, 14800; ν_{max}; a broad band at 1740 cm^{-1}, with three peaks at 1755, 1725 and 1685 cm^{-1}, two weak bands at 1628 and 1600 cm^{-1}. (Found: C, 69·05; H, 6·16; O, 24·69; Calc. for $C_{15}H_{16}O_4$: C, 69·21; H, 6·20; O, 24·59%).

Dihydroisomexicanin I (III). A solution of mexicanin I (300 mg) in ethyl acetate (150 ml) was hydrogenated with 10% palladium-in-charcoal catalyst (80 mg). The uptake of hydrogen ceased after 1 equivalent was absorbed. The catalyst was filtered and the solution evaporated to dryness. The oily residue crystallized from ether, yielding brilliant plates (255 mg), m.p. 136–139°. Further crystallizations from acetone–hexane raised the m.p. to 144–146°, (positive Zimmermann test); $[\alpha]_D$ +150·4°; λ_{max}; 222, 290 mμ; ε, 7000, 40; ν_{max} 3520, 1770, 1740 cm^{-1} and a weak band at 1610 cm^{-1}. Rotatory dispersion (in dioxane), $[\alpha]_{700}$ +173°, $[\alpha]_{589}$ +169°, $[\alpha]_{330}$ +1734·6°, $[\alpha]_{317\cdot5}$ +2792·3°, $[\alpha]_{300}$ +611·53°. $[\alpha]_{277\cdot5}$ −1996°, $[\alpha]_{265}$ −1407·7°. (Found: C, 67·93; H, 7·75; O, 24·44; Calc for $C_{15}H_{20}O_4$: C, 68·16; H, 7·63; O, 24·21%).

Dehydrodihydroisomexicanin I (IV). Dihydroisomexicanin I (III; 170 mg) was dissolved in acetic acid (6 ml) and mixed with a solution of chromium trioxide (150 mg) in water (1 ml) and acetic acid (4 ml). The mixture was left at room temp for 80 min. Diluted then with water and extracted with chloroform. The chloroformic solution was washed with water, dried on anhydrous sodium sulfate and evaporated to dryness. The residue was crystallized from acetone–hexane yielding prismatic needles (110 mg), m.p. 170–174°. Further crystallizations from acetone–ether raised the m.p. to 173–175°; $[\alpha]_D$ +184°; λ_{max} 243 mμ; ε, 10736; ν_{max}; 1760, a relative weak band at 1690 cm^{-1} and a weak band at 1635 cm^{-1}. (Found: C, 68·85; H, 7·11; O, 24·52; Calc. for $C_{15}H_{18}O_4$: C, 68·68; H, 6·92; O, 24·40%).

Dehydrodesacetyldihydroisotenulin (V), *by reduction of dehydrodihydroisomexicanin* I (IV). To a solution of dehydrodihydroisomexicanin I (IV; 100 mg) in acetic acid (10 ml), powdered zinc (800 mg) was added. The mixture was refluxed for 3 hr. The zinc was filtered, the solution diluted with water

* M.p's. are uncorrected. Rotations were determined at 20° in chloroform. The I.R. spectra were determined in chloroform solution on a Perkin–Elmer double beam spectrophotometer. The U.V. absorption spectra were run in 95% ethanol solution in a Beckman DK2 spectrophotometer. The microanalyses were performed by Dr. Franz Pascher, Bonn, Germany.

and extracted with chloroform. The chloroformic solution was washed with water, 5% sodium hydroxide solution was water again. It was dried on anhydrous sodium sulfate and evaporated to dryness. The oily residue crystallized from ether, yielding needles m.p. 150–156° (60 mg). Several crystallizations from acetone–ether raised the m.p. to 168–171°; $[\alpha]_D$ +20°; ν_{max}; a broad band at 1755 cm^{-1}, a relatively weak band at 1706. Identity with dehydrodesacetyldihydroisotenulin,[6,7] was stablished by comparison of I.R. spectra and thin-layer chromatography. The difference in m.p. with dehydrodesacetyldihydroisotenulin[11] apparently are due to solvation, we have obtained analytical samples with different m.p. (see below). (Found: C, 68·01; H, 7·66; O, 24·20; Calc. for $C_{15}H_{20}O_4$: C, 68·16; H, 7·63; O, 24·21%).

Dehydrodesacetyldihydroisotenulin (V), *by reduction of dehydroisomexicanin* I (II). With 100 mg of the diketone (II), the reduction was carried out in the same way described in the above experiment. There were obtained 45 mg of dehydrodesacetyldihydroisotenulin (V), m.p. 147–149°; $[\alpha]_D$ +22°; it was identified with the product obtained in the above experiment.

Desacetyldihydroisotenulin (VIa). To a solution of mexicanin I (500 mg) in benzene (80 ml), were added 2 ml piperidine and 2 ml benzylmercaptan. The mixture was refluxed for 6 hr; washed then with dil. hydrochloric acid and water. The solution was dried on anhydrous sodium sulfate and evaporated to dryness. The residual oil (760 mg) was dissolved in ethanol (70 ml). Raney nickel freshly prepared (approx. 7 g) was added, and the mixture refluxed for 8 hr with mechanical stirring. The nickel was then filtered and the solution evaporated to dryness. Crystallization of the oily residue from ether–hexane, afforded needles (125 mg), m.p. 186–188°. Several crystallizations from acetone–ether furnished the analytical sample, m.p. 194–196°; $[\alpha]_D$ +139°; ν_{max}; 3580, 1770 and 1740 cm^{-1}. Mixed m.p. determination with desacetyldihydroisotenulin showed no depression and the I.R. spectra were identical. (Found: C, 67·67; H, 8·20; O, 23·97; Calc. for $C_{15}H_{22}O_4$: C, 67·64; H, 8·33; O, 24·03%).

A solution of 60 mg of desacetyldihydroisotenulin (VIa) in 1 ml of acetic anhydride and 1 ml pyridine was heated for 1 hr on the steambath. The solution was poured in water and extracted with chloroform. The chloroformic extract was washed with dil. hydrochloric acid, water, dil. sodium hydroxide solution and water again. The solution was dried on anhydrous sodium sulfate and evaporated to dryness. Crystallization of the oily residue from ether yielded dihydroisotenulin (VIb), m.p. 147–148° (35 mg). The analytical sample showed m.p. 149–150° (prisms from ether–hexane). $[\alpha]_D$ +101°; ν_{max}; a broad band at 1770 cm^{-1}. (Found: C, 66·40; H, 7·97; O, 25·93; Calc. for $C_{17}H_{24}O_5$: C, 66·21; H, 7·84; O, 25·95%).

Dehydrodesacetyldihydroisotenulin (V), *by oxydation of desacetyldihydroisotenulin* (VIa). The tetrahydroderivative (VIa) (40 mg) was dissolved in acetic acid and oxydized following the same procedure used in previous experiments. Crystallization from acetone–hexane yielded needles, m.g. 145–147°. It proved to be identical with the products obtained by zinc in acetic acid reduction of dehydroisomexicanin I (II) and dehydrodihydromexicanin I(IV).

Alkaline treatment of mexicanin I (Ia). A solution of mexicanin I (140 mg) in methanol (20 ml) was mixed with potassium hydroxide (140 mg) dissolved in water (2 ml). The mixture was refluxed for 3 min and left at room temp for 30 min. It was then acidified with acetic acid and concentrated to a small volume, diluted with water and extracted with chloroform. The chloroformic extract was washed with water and concentrated. Neomexicanin I (VIIa) crystallized upon addition of ether, yielding brilliant plates (70 mg), m.p. 250–256°. Several crystallizations from chloroform–methanol raised the m.p. to 259–263°; $[\alpha]_D$ +10°; λ_{max}; 210, 239 mμ; ε, 9900, 15000; ν_{max}; 3330, 1770, 1698 and 1635 cm^{-1}. Rotatory dispersion (in dioxane), $[\alpha]_{700}$ +30·49°, $[\alpha]_{589}$ +23·3°, $[\alpha]_{345}$ +559·6°, $[\alpha]_{330}$ +502·24°, $[\alpha]_{320}$ +658·29°, $[\alpha]_{321}$ +306·7°, $[\alpha]_{318}$ +319·28°, $[\alpha]_{287·5}$ −493·27°. (Found: C, 68·44; H, 7·17; O, 24·53; Calc. for $C_{15}H_{18}O_4$: C, 68·68; H, 6·92; O, 24·40%).

The mother liquor from the first crystallization was evaporated to dryness. The oily residue crystallized from acetone–hexane furnishing methoxydihydroneomexicanin I (VIII), m.p. 163–165°. The analytical sample showed m.p. 168–170° (needles from acetone–hexane); $[\alpha]_D$ −27°; λ_{max} 240 mμ; ε, 12900; ν_{max}; 3330, 1770, 1690 and 1630 cm^{-1}. (Found: C, 65·56; H, 7·38; O, 27·10; Calc. for $C_{16}H_{22}O_5$: C, 65·29; H, 7·54; O, 27·17%).

To a solution of 300 mg of mexicanin I in 50 ml of t-butyl alcohol were added 200 mg potassium hydroxide in 18 ml water, the mixture was heated on the steambath for 5 min and left at room temp for additional 20 min. Acidified then with acetic acid and evaporated to a small volume *in vacuo*. When the t-butyl alcohol was eliminated neomexicanin I crystallized. The precipitate was collected

and recrystallized from chloroform–methanol yielding neomexicanin I (120 mg), m.p. 255–262°. The analytical sample showed m.p. 262–265°. Comparison of this product with that obtained from the alkaline hydrolysis in methanol by the standard methods, proved to be identical.

Neomexicanin I *acetate* (VIIb). Showed m.p. 170–172° (Prisms from acetone–ether) $[\alpha]_D$ +3°; λ_{max} 210–212, 238 ,304–312 mμ; ε, 11000, 14800, 67. (Found: C, 66·90; H, 6·85; O, 26·37; Calc. for $C_{17}H_{22}O_5$: C, 67·09; H, 6·62; O, 26·29%).

Hydrogenation of mexicanin I *acetate*. A solution of the lactone (500 mg) in ethyl acetate (60 ml) was hydrogenated with Adams catalyst (60 mg). Two equivalents of hydrogen were absorbed in 4 hr. The catalyst was filtered and the solution evaporated to dryness. Crystallization of the oily residue from ether yielded 11-epidihydroisotenulin (260 mg), m.p. 106–108°. The analytical sample showed m.p. 109° (small prisms from ether–hexane); $[\alpha]_D$ +48°; ν_{max} 1770 and 1730 cm^{-1}. (Found: C, 66·11; H, 7·94; O, 25·87; Calc. for $C_{17}H_{24}O_5$: C, 66·21; H, 7·84; O, 25·95%).