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THE CONSTITUENTS OF *HELENIUM AROMATICUM* (HOOK) BAILEY

THE STRUCTURES OF AROMATIN AND AROMATICIN[1]

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Abstract—Helenalin, Mexicanin I and two new sesquiterpene lactones; aromatin and aromaticin were isolated from the Chilean plant Helenium aromaticum. The structures of the new lactones have been established. Aromatin is 6-desoxyhelenalin and aromaticin is 6-desoxymexicanin I.

Helenium aromaticum (Hook) Bailey[2,3] is a bitter herb occurring commonly in the central part of Chile. It is known popularly as "manzanilla del campo". Several related sesquiterpene lactones have been isolated from Helenium species collected in different regions of North America, such as helenalin,[4,9] tenulin,[5,8] mexicanins A[6,7,9] and C[6,7,10] etc. We were interested in the chemical study of this plant[11] which is distributed in the southern part of America, since the knowledge about its constituents might contribute to establish the phylogenetical relationships among helenium species occurring in very distant geographical environment.

Extensive chromatography of the chloroformic extract of *H. aromaticum* furnished from the more polar fractions a crystalline mixture which was separated in two components by fractional crystallization. The more soluble product m.p. 172–174°, proved to be identical with helenalin[9] (III). The less soluble substance, m.p. 260–263° was identified as mexicanin I.[12] The recent results of X-ray analysis of bromoisotenulin by Rogers and Mazharul-Haque[13] combined with the optical rotatory dispersion evidence[10] show that bromoisotenulin is represented by formula I. Therefore the relative stereochemistry of several lactones correlated with tenulin (II) could be

[1] Contribution No. 154 from the Instituto de Química (U.N.A.M.)
[2] Sinopsis de la Flora Chilena, Carlos Muñoz Pizarro, Ediciones de la Universidad de Chile, 1959.
[3] We are indebted to the botanist, Miss Eugenia Navas (Universidad Católica de Santiago) for the identification of the plant.
[4] E. P. Clark, *J. Amer. Chem. Soc.* **58**, 1982 (1936).
[5] E. P. Clark, *J. Amer. Chem. Soc.* **61**, 1836 (1939).
[6] A. Romo de Vivar and J. Romo, *Chem. & Ind.*, 882 (1959).
[7] A. Romo de Vivar and J. Romo, *Ciencia, Mex.*, **21**, (1), 33 (1961).
[8] W. Herz, W. A. Rohde, K. Rabindran, P. Jayaraman and N. Viswanathan, *J. Amer. Chem. Soc.* **84**, 3857 (1962).
[9] W. Herz, A. Romo de Vivar, J. Romo and N. Viswanathan, *J. Amer. Chem. Soc.* **85**, 19 (1963).
[10] W. Herz, A. Romo de Vivar, J. Romo and N. Viswanathan, *Tetrahedron* **19**, 1359 (1963).
[11] A preliminary report of part of this work have already appeared: J. Romo, P. Joseph-Nathan and Fernando Díaz A., *Chem. & Ind.* in press.
[12] E. Domínguez and J. Romo, *Tetrahedron* **19**, 1415 (1963).
[13] D. Rogers and Mazhar-ul-Haque, *Proc. Chem. Soc.* 92 (1963).

defined.[10] Helenalin, which differs from tenulin at the C_5 and C_8 asymmetrical centers[14] can be formulated as IIIa Mexicanin I a structural isomer of helenalin with the C_1, C_5, C_6, C_7, C_8 and C_{10} asymmetrical centers oriented as in tenulin corresponds formula IVa. From the less polar fractions of the chromatogram there were isolated two isomeric lactones with very similar chemical and spectroscopic properties, which we have named aromatin and aromaticin. Their empirical formulae ($C_{15}H_{18}O_3$) and spectroscopical features suggest a close relationship with ambrosin[15–17] (V), which could be confirmed subsequently.

Aromatin, m.p. 159–160°, $[\alpha]_D$ −6° does not form an acetate, the UV spectrum (λ max 215 mμ; ε, 15000) and the IR bands at 1760, 1660 (unsaturated five membered lactone), at 1710 and 1578 cm^{-1} (cyclopentenone) points to the presence of two chromophores; an exocyclic methylene group conjugated with a lactone and a cyclopentenone, similar to those found in the structures of several "abnormal" guaianolides like ambrosin[15,16] (V) and helenalin[9] (IIIa). This was supported by the following evidence. Aromatin forms a dipyrazoline when its methanolic solution is treated with ethereal diazomethane. The optical rotary dispersion curve of aromatin shows a negative Cotton effect of the same type of those of helenalin and tenulin,[18] though of lesser amplitude, suggesting a similar ketonic chromophore and identical stereochemistry at the ring junction. The NMR spectrum[19] indicates the presence of four vinyl protons; three pairs of doublets centered at 7·48 ppm (J = 1·5 cps) (the relative intensity of the first doublet at 7·68 ppm is very small) ascribed to the proton at C-3. The signals of the proton at C-2 are partially superimposed to those of one hydrogen of the exocyclic methylene group. There are three doublets centered at 6·13 ppm (intensity two protons) and two doublets at 5·66 ppm (J = 2·5 cps) and at 5·48 ppm (J = 3 cps) (intensity one proton).

Catalytic hydrogenation of aromatin saturated the cyclopentenone, affording a dihydroderivative, the other double bond migrated to endocyclic conjugation with the lactone, since the product showed a λ max at 218 mμ (ε, 15800) and resisted further hydrogenation. This behaviour is observed frequently in the hydrogenation of similar lactones.[9,17] The IR spectrum had a broad band at 1740 (γ-lactone and cyclopentanone) and at 1675 cm^{-1} (C—C double bond).

The structure of aromatin was elucidated when dihydroisoaromatin was indentified with 6-desoxydihydroisohelenalin (VI) prepared according to the method of Herz *et al.*[20] by treatment of tetrahydrohelenalin mesilate (VIIb) with 2,6 lutidine. Therefore the structure of aromatin corresponds to that of 6-desoxyhelenalin (VIII) with the same asymmetrical centers at C_1, C_5, C_8, C_{10} and the same lactone closure at C_8. The asymmetrical center at C_7 most probably has also the same configuration as in helenalin and several other lactones recently correlated.[10]

When the crude adduct of aromatin and benzylmercaptan was desulfurized with Raney nickel as in the case of mexicanin I[12] (IVa), an oily mixture was obtained.

[14] W. Herz and R. B. Mitra, *J. Amer. Chem. Soc.* **80**, 4876 (1958).
[15] L. Bernardi and G. Büchi, *Experientia* **13**, 466 (1957).
[16] W. Herz, M. Miyazaki and Y. Kishida, *Tetrahedron letters* No. 2, 82 (1961).
[17] W. Herz, H. Watanabe, M. Miyazaki and Y. Kishida, *J. Amer. Chem. Soc.* **84**, 2601 (1962).
[18] C. Djerassi, J. Osiecki and W. Herz, *J. Org. Chem.* **22**, 1361 (1957).
[19] The NMR spectra were run on a Varian A-60 spectrometer, in deuterochloroform solution, using tetramethylsilane as internal standard.
[20] W. Herz, P. Jayaraman and H. Watanabe, *J. Amer. Chem. Soc.* **82**, 2276 (1960).

After chromatographic purification only a small amount of a crystalline product was obtained. This derivative corresponds to a hexahydroaromatin (IX) in which the original keto group was reduced to a secondary alcohol, since the IR spectrum exhibited a hydroxyl band at 3600 cm^{-1}. Chromium trioxide oxydation of the combined oily fractions from the chromatogram (very probably a mixture of C_4-estereoisomers and ketonic material) afforded an oily tetrahydroaromatin (X). It had a IR broad band at 1750 cm^{-1} (γ-lactone and cyclopentanone).

Aromaticin showed m.p. 232–234°, $[\alpha]_D$ +18°. The nature of the three oxygen atoms and of the two C—C double bonds may be interpreted from the UV spectrum (λ max 215 mμ; ε, 15,500) and the IR bands at 1760 and 1670 (unsaturated γ-lactone), 1710 and 1585 cm^{-1} (cyclopentenone, as involved in two chromophores similar to those of aromatin (VIII). The optical rotatory dispersion curve of aromaticin shows also a negative Cotton effect. Aromaticin affords a dipyrazoline on treatment with diazomethane in methanol–ether solution. Bromination of aromaticin furnished a dibromoderivative (XI), in which the bromine was added to the double bond of the cyclopentenone. The exocyclic methylene group is responsible for the UV maximum at 210 mμ, (ε, 6100). The IR spectrum exhibited a band at 1755 cm^{-1} (cyclopentanone and unsaturated γ-lactone) and a band of double bond at 1670 cm^{-1}. The NMR spectrum of aromaticin indicates the presence of the cyclopentenone vinyl protons, a pair of doublets at 7·68 and 7·58 ppm (J = 2 cps) (α-hydrogen). The β hydrogen exhibited a doublet at 6·05 ppm (J = 3 cps); the other one at 6·14 ppm (J = 3 cps) is superimposed with one of the two doublets displayed by the hydrogens of the exocyclic methylene group centered at 6·14 and 5·5 ppm (J = 3 cps).

When aromaticin was hydrogenated in the presence of palladium-on-charcoal catalyst, there was obtained dihydroisoaromaticin (λ max 220 mμ; ε, 11,000) IR bands at 1740 (γ-lactone and cyclopentanone) and at 1670 cm^{-1} (C—C double bond). This product proved to be identical with 6-desoxydihydroisomexicanin I (XII), obtained by 2,6-lutidine treatment of desacetyldihydroisotenulin mesilate (XIIIb). Therefore aromaticin must be formulated as 6-desoxymexicanin I (XIV) with the same asymmetrical centers at C_1, C_5, C_8, C_{10} and identical lactone closure at C_8 as in mexicanin I (IVa) and tenulin (II) (see ref. 12). We suggest on biogenetical grounds for the asymmetrical center at C-7, the same configuration present in mexicanin I.

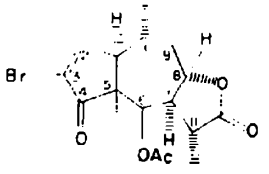
Therefore aromatin (VIII) and aromaticin (XIV) possess the same structure differing only at the C-8 asymmetrical center, as other azulogenic lactone isolated from Helenium species already correlated, their lactone is closed at C-8.

As in the case of aromatin, aromaticin gives rise to a hexahydroderivative (XV) by desulfurization with Raney nickel of its benzylmercaptan adduct. It showed in the IR spectrum bands at 3600 (hydroxyl group) and at 1770 cm^{-1} (γ-lactone). Chromium trioxide oxydation furnished tetrahydroaromaticin m.p. 132–134° (XVI). The IR spectrum had bands at 1770 (γ-lactone) and at 1740 cm^{-1} (cyclopentanone).

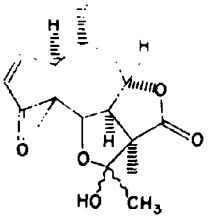
We have found that desulfurization of the benzylmercaptan adduct of helenalin gives rise to dihydromexicanin C[8] (XVII), which has opposite configuration at C-11 in regard to tetrahydrohelenalin (VIIa), obtained by catalytic hydrogenation of helenalin (IIIa). Desacetyldihydroisotenulin (XIIIa) has been obtained also by desulfurization of the toluenethiol adduct of mexicanin I.[12] It is known that dihydromexicanin C (XVII) and dihydroisotenulin (XIIIc) [and desacetyldihydroisotenulin (XIIIa)] possess identical asymmetric center at C-11.[10] Therefore we tentatively assign

to the hexahydro and tetrahydroderivatives of aromatin and aromaticin (X; XVI), the same configuration at C-11 present in dihydromexicanin C (XVII) and desacetyldihydroisotenulin (XIII) since they were obtained by identical procedure.

It is interesting to comment that helenalin (IIIa) and mexicanin I (IVa) were isolated previously[12] from *H. mexicanum* distributed in Oaxaca (Mexico). We could not isolate from this plant the other lactones present in *H. mexicanum*,[6,7] collected in the neighborhood of Mexico City, particularly mexicanin E, which is found in comparative large amounts through all the vital cycle of the plant.[7] Therefore we feel it would be advisable to do a revision of the botanical classification of the Helenium occurring in Oaxaca since from the chemical point of view it is more related to *H. aromaticum*.



I



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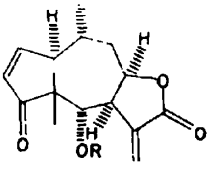
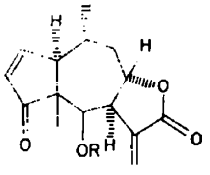
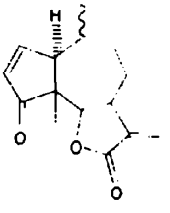


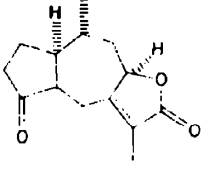
III a; R = H
b; R = Ac



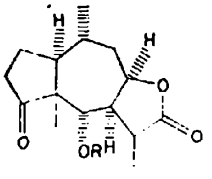
IV a; R = H
b; R = Ac



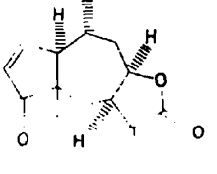
V



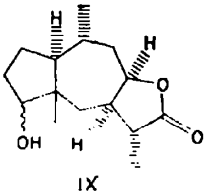
VI



VII a; R = H
b; R = CH_3-SO_2-



VIII

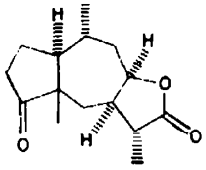


IX

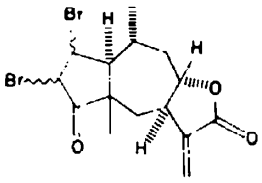
EXPERIMENTAL[21]

Isolation of the lactones. Air dried *H. aromaticum* collected in the vicinity of Santiago, Chile in November–December (at the end of the spring) weight 500 g (whole plant) was crushed and extracted

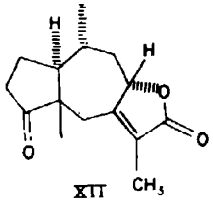
[21] M.ps. are uncorrected. UV spectra were run on a Beckman DK2 spectrophotometer in 95% ethanol solution; IR spectra in chloroform solution on a Perkin–Elmer double beam spectrophotometer. Rotations were determined in chloroform solution at 20° unless noted otherwise. The microanalyses were performed by Dr. Franz Pascher, Bonn, Germany. The alumina used was washed with ethyl acetate and dried at 100° *in vacuo*.



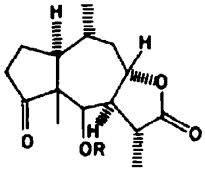
X



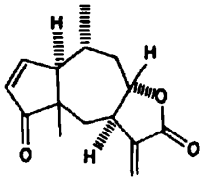
XI



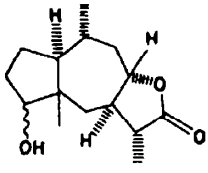
XII



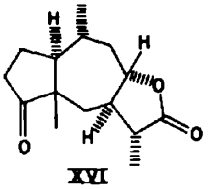
XIII a; R = H
b; R = CH_3-SO_2-
c; R = Ac



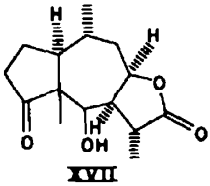
XIV



XV



XVI



XVII

by refluxing with 3 l. chloroform for a period of 8 hr. The extraction was repeated 4 times. The combined chloroformic extracts were evaporated to dryness. The residue (55 g) was dissolved in 700 ml ethanol and mixed with a solution of lead acetate (30 g) in 1·1 l. water. The mixture was left 3 hr at room temp. The clear solution was decanted from a semisolid residue and extracted 3 times ($CHCl_3$; 1 l.). The combined extracts were evaporated to dryness. The oily residue (31 g) was dissolved in benzene-hexane 3:1 and chromatographed over alumina (600 g). Several fractions eluted with benzene-hexane 3:1 and 2:1, crystallized. They were combined and recrystallized from acetone yielding aromaticin (XIV) (450 mg), m.p. 225–229°. The mother liquors afforded 110 mg, m.p. 210–212°. The analytical sample was obtained by repeated crystallizations from acetone, prisms m.p. 232–234°, $[\alpha]_D$ +18°; λ max 215, 320 mμ; ε, 15500, 50. ν max 1760, 1710, 1670 and 1585 cm^{-1}. Rotatory dispersion (in dioxane); $[\alpha]_{600}$ −175°; $[\alpha]_{375}$ −510°; $[\alpha]_{370}$ −565°; $[\alpha]_{365}$ −510°; $[\alpha]_{330}$ +835°. (Found: C, 72·88; H, 7·35; O, 19·52. mol. wt. (Rast) 274; Calc. for $C_{15}H_{16}O_3$: C, 73·15; H, 7·37; O, 19·48%).

The mother liquors crystallized from ether–hexane furnishing aromatin (VIII; 360 mg) m.p. 158–159°. The analytical sample showed m.p. 159–160° (long needles from acetone–hexane), $[\alpha]_D$ −6° λ max 215, 320 mμ; ε, 15,000, 50; ν max 1760, 1710, 1660 and 1578 cm^{-1}. Rotatory dispersion (in dioxane); $[\alpha]_{600}$ −296°; $[\alpha]_{365}$ −685°; $[\alpha]_{350}$ −740°; $[\alpha]_{330}$ −370°; $[\alpha]_{330}$ +860°. (Found: C, 72·89; H, 7·25; O, 19·33. mol. wt. (Rast) 267; Calc. for $C_{15}H_{16}O_3$: C, 73·15; H, 7·37; O, 19·48%).

Most of the fractions eluted with benzene and benzene–chloroform 5:1, 4:1 and 3:1 crystallized. Recrystallization from methanol yielded mexicanin I (IVa; 1·015 g), m.p. 260–263°, $[\alpha]_D^{20}$ +57° (in pyridine), λ max 215, 319 mμ; ε, 155,000, 48; it showed no depression on admixture with an authentic sample[12] and the IR spectra were superimposable.

The acetate (IVb) showed m.p. 200–203° (needles from acetone–hexane), $[\alpha_D]$ +28°, λ max 214, 322 mμ; ε, 14100, 49; it was identified with an authentic sample by the standard methods.

From the mother liquors left after the crystallization of mexicanin I, there was obtained helenalin (IIIa; 210 mg), m.p. 165–168°. Recrystallization from acetone–ether yielded prisms m.p. 172–174°, $[\alpha]_D$ −76°, λ max 219, 318 mμ; ε, 11,800, 47; it was identified with an authentic sample by the standard methods. The acetate (IIIb) showed m.p. 180–182°, $[\alpha]_D$ −99°, λ max 215 mμ; ε, 14,200.

Aromatin dipyrazoline. A solution of aromatin (VIII; 150 mg) in methanol (20 ml) was mixed with 30 ml of an ethereal solution of diazomethane (prepared with 1 g of N-nitrosomethylurea), the dipyrazoline began to crystallize in a few min. After 3 hr at room temp the excess of diazomethane was eliminated by addition of acetic acid and the precipitate collected. The product (110 mg) showed m.p. 150–151° dec $[\alpha]_D$ +686° (in pyridine); ν max 1780 and 1750 cm^{-1}. (Found: C, 61·73; H, 6·72; O, 14·53; N, 16·94; Calc. for $C_{17}H_{22}O_3N_4$: C, 61·80; H, 6·71; O, 14·53; N, 16·96%).

Dihydroisoaromatin (VI). Aromatin (VIII; 400 mg) was dissolved in ethyl acetate (50 ml) and hydrogenated with 10% Pd–C (80 mg). The absorption of hydrogen ceased after 2 hr. The catalyst was filtered and the solution evaporated to dryness. The oily residue crystallized from acetone–hexane yielding prismatic needles (85 mg) m.p. 139–141°; $[\alpha]_D$ +33·8°, λ max 218, 290 mμ; ε, 15,800, 49; ν max 1740 and 1675 cm^{-1}. (Found: C, 72·31; H, 8·15; O, 19·37; Calc. for $C_{15}H_{20}O_3$: C, 72·55; H, 8·12; O, 19·33%).

Tetrahydrohelenalin mesilate (VIIb). It was prepared following the method described by Herz *et al.*[20] Prisms from acetone–hexane, m.p. 126–127°; $[\alpha]_D$ +91°. ν max a broad band with two peaks at 1770 and 1740 cm^{-1}. (Found: C, 55·63; H, 7·18; O, 27·95; S, 9·33; Calc. for $C_{16}H_{24}O_6S$: C, 55·77; H, 7·02; O, 27·91; S, 9·30%.).

6-*Desoxydihydroisohelenalin* (VI). Tetrahydrohelenalin mesilate (VIIb; 700 mg) was treated with 2,6-lutidine following directions previously described.[20] The lactone (VI) showed m.p. 139–140° (prismatic needles from acetone–hexane), $[\alpha]_D$ +33·4°; λ max 218, 286 mμ; ε, 16200, 83; mixed m.p. with dihydroisoaromatin showed no depression and the IR spectra were superimposable.

Aromaticin dipyrazoline. A solution of aromaticin (150 mg) in 30 ml of methanol was treated with ethereal diazomethane as in the previous case. The dipyrazoline crystallized after few min. Recrystallization from chloroform–hexane yielded prisms (135 mg), m.p. 192–194° dec, $[\alpha]_D$ +308·7° (in pyridine); ν max 1780 and 1748 cm^{-1}. (Found: C, 61·57; H, 6·85; O, 14·53; N, 16·89; Calc. for $C_{17}H_{22}O_3N_4$: 61·80; H, 6·71; O, 14·53; N, 16·96%).

2,3-*Dibromodihydroaromaticin* (XI). Aromaticin (XIV; 200 mg) dissolved in 8 ml of acetic acid was treated with a solution of 5% bromine solution in acetic acid, until persisted a pale orange colour. The solution was diluted with water, extracted with ether, the ethereal extract was washed with water, dil. NaOH aq. and water again, dried and concentrated to a small volume, hexane, was added. The dibromoderivative (XI) crystallized. It showed m.p. 143–144° dec. Recrystallization from acetone–ether afforded prismatic needles m.p. 144–145° dec $[\alpha]_D$ −69°, λ max 210, 322 mμ; ε, 6100, 96. ν max 1755 (γ-lactone and cyclopentanone) and 1670 cm^{-1} (C—C double bond). (Found: C, 44·45; H, 4·56; O, 11·88; Br, 39·59; Calc. for $C_{15}H_{18}O_3Br_2$: C, 44·34; 4·46; O, 11·81; Br, 39·38%).

Dihydroisoaromaticin (XII). Aromaticin (XIV; 400 mg) was hydrogenated following the same procedure used in aromatin (VIII). Crystallization from acetone–hexane furnished prismatic needles (280 mg) m.p. 130–133°. The analytical sample was obtained by further recrystallizations from acetone–hexane, m.p. 132–133°; $[\alpha]_D$ +176°; λ max 220, 291 mμ; ε, 11,000, 45; ν max 1740 and 1670 cm^{-1}. (Found: C, 72·79; H, 8·20; O, 19·43; Calc. for $C_{15}H_{20}O_3$: C, 72·55; H, 8·12; O, 19·33%).

Desacetyldihydroisotenulin mesilate (XIIIb). Desacetyldihydrodisotenulin (XIIIa[22]; 500 mg) was mesilated as in the previous case. Crystallization from acetone–hexane yielded prisms (370 mg), m.p. 190–192° dec. Further crystallization from the same solvents raised the m.p. to 196–197° dec $[\alpha]_D$ +90·8°, ν max a broad band with two peaks at 1700 and 1740 cm^{-1}. (Found: C, 55·56; H, 7·09; O, 28·09; S, 9·17; Calc. for $C_{16}H_{24}O_6S$: C, 55·77; H, 7·02; O, 27·91; S, 9·30%).

6-*Desoxydihydroisomexicanin* I (XII). A solution of desacetyldihyroisotenulin mesilate (XIIIb; 250 mg) in 2,6 lutidine (10 ml) was refluxed for 24 hr. It was then poured in 20% hydrochloric acid (60 ml) and extracted with chloroform. The organic layer was washed with water, dried (Na_2SO_4) and evaporated to dryness. The oily residue was chromatographed over alumina (3 g). The fractions eluted with benzene–hexane 1:1, 2:1 and 3:1, crystallized. They were combined and recrystallized from acetone–hexane, yielding prismatic needles (70 mg), m.p. 135–136°, $[\alpha]_D^{20}$ +179·5°, λ max 221,

[22] Obtained by desulfurization of the adduct of benzylmercaptan with mexicanin I (see ref. 12).

285 mμ; ε, 14,400, 58. This product was identified with dihydroisoaromaticin (XII) by the standard methods. (Found: C, 72·45; H, 8·32; O, 19·48; Calc. for $C_{15}H_{20}O_3$: C, 72·55; H, 8·12; O, 19·33%).

Hexahydroaromatin (IX). To a solution of aromatin (300 mg) in benzene (25 ml), benzylmercaptan (1 ml) and piperidine (1 ml) were added. The mixture was refluxed for 6 hr, washed then with 10% HCl, dil. NaOHaq. evaporated to dryness. The oily residue was dissolved in ethanol (60 ml), freshly prepared Raney Nickel[22] (5 g) was added and the mixture refluxed for 16 hr. The nickel was filtered and the solvent evaporated. The oily residue dissolved in hexane-25% benzene and chromatographed over alumina (6 g). The fractions eluted with benzene-30, 20 and 10% hexane, were partially crystallized. They were combined and recrystallized from acetone–ether yielding prisms (70 mg), m.p. 172–174°; ν max 3600 and 1770 cm^{-1}. (Found: C, 71·13; H, 9·44; O, 19·29; Calc. for $C_{15}H_{24}O_3$: C, 71·39; H, 9·59; O, 19·02%).

Tetrahydroaromatin (X). The oily fractions from the above chromatogram and the mother liquors from the crystallization of hexahydroaromatin (IX) were combined (190 mg) dissolved in acetic acid (8 ml) and treated with a solution of chromium trioxyde (160 mg) in 1 ml water and 3 ml acetic acid. The mixture was left for 1 hr at room temp, diluted then with water and extracted with chloroform. The organic layer was washed with water, 5% NaOHaq. and water again, dried and evaporated. The oily residue did not crystallize even after distillation in vacuo. $[\alpha]_D$ +121°; ν max a broad band at 1750 cm^{-1} (it did not show hydroxyl band). (Found: C, 71·74; H, 9·11; O, 19·26; Calc. for $C_{15}H_{22}O_3$: C, 71·97; H, 8·86; O, 19·17%).

Hexahydroaromaticin (XV). Aromaticin (XIV; 300 mg) was treated with benzylmercaptan and piperidine. The adduct obtained in this way was desulfurized following the same method described previously. Hexahydroaromaticin (XV) crystallized from ether–hexane yielding prisms (130 mg), m.p. 128–131°. Further crystallizations from acetone–hexane raised the m.p. 140–142°; $[\alpha]_D$ +49°; ν max 3600 and 1770 cm^{-1}. (Found: C, 71·27; H, 9·48; O, 19·07; Calc. for $C_{15}H_{24}O_3$: C, 71·39; H, 9·59; O, 19·02%).

Tetrahydroaromaticin (XVI). Hexahydroaromaticin (XV; 60 mg) in acetic acid (4 ml) was treated with chromium trioxide (60 mg) in 0·3 ml water and 2 ml acetic acid. It was then proceded as in the above described oxydation. Tetrahydroaromaticin (XVI) showed m.p. 132–134° (long needles from ether–hexane), yield 45 mg $[\alpha]_D$ +175°; ν max 1770 and 1740 cm^{-1} (it did not show hydroxyl band). (Found: C, 71·73; H, 8·93; O, 19·19; Calc. for $C_{15}H_{22}O_3$: C, 71·97; H, 8·86; O, 19·17%).

Dihydromexicanin C (XVII). To a solution of helenalin (IIIa; 1 g) in benzene (80 ml) was added benzylmercaptan (3 ml) and piperidine (3 ml), refluxed 6 hr. The oily adduct obtained was desulfurized following the same method described above for similar cases. Dihydromexicanin C (XVII) showed m.p. 161–164° (prisms from ether), yield 305 mg. Further crystallizations from acetone–hexane raised the m.p. to 172–174°; $[\alpha]_D$ +115·3°; it was identified with an authentic specimen by the standard methods. The acetate showed m.p. 117–118°, $[\alpha]_D$ +116°.

[22] *Org. Syntheses*, 21, 15 (1941).