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THE CONSTITUENTS OF *ZALUZANIA AUGUSTA*

THE STRUCTURES OF ZALUZANINS A AND B[1]

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Abstract—The structures of zaluzanins A and B, constituents of *Zaluzania augusta* have been established as sesquiterpene lactones of the guaiane series.

Zaluzania augusta (Lag.) Schultz Bip. a Compositae of the tribe *Heliantheae* is widely distributed in Mexico. From the extract of the aereal part of the shrub we have isolated two components named zaluzanins A and B.

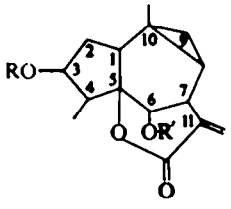
Zaluzanin A (Ia) is a crystalline product, m.p. 265°, $[\alpha]_D$ −10°, eluted from the more polar fractions of the chromatogram. The analysis is correct for $C_{15}H_{20}O_4$; two secondary hydroxyl groups (IR band at 3400 cm $^{-1}$) may be acetylated under basic conditions. The presence of a 6 (or more) membered lactone conjugated with an exocyclic methylene group is deduced from the following evidence. An alkaline methanolic solution of Ia does not form a precipitate on dilution with water but only upon acidification. Zaluzanin A (Ia) shows in the UV spectrum a max at 210 mμ; ϵ 9815 and has IR bands at 1695 and 1638 cm $^{-1}$. Treatment of Ia with ethereal diazomethane afforded the pyrazoline (II). Furthermore, dehydrozaluzanin A (IX) liberates formaldehyde on ozonolysis. Catalytic hydrogenation of zaluzanin A (Ia) yields a dihydro derivative (IIIa) which resists further hydrogenation even under drastic conditions. Therefore the lactone (Ia) appears to be a tricyclic product.

The NMR spectrum of zaluzanin A diacetate (Ic)[2] exhibits two low field singlets at 6·20 and 5·60 corresponding to the exocyclic methylene protons. A triplet centered at 5·28 and a doublet (J = 3 c/s) at 5·00 are attributed to the protons attached to the carbons bearing the acetoxy groups. A tertiary hydroxyl group appears to be involved in the lactone closure due to the fact that the NMR spectrum of Ic does not show the typical low field signal of the proton on the carbon carrying the ethereal oxygen of the lactone.[3] A doublet at 3·23 (J = 3 c/s) is assigned to an allylic proton. In the methyl region, the acetyl groups appear as two superimposed singlets (6 H) at 2·08. A singlet at 1·05 and a doublet (J = 7 c/s) centered at 0·90 are ascribed to a tertiary and a secondary methyl group, respectively. Three protons which in the NMR spectrum of Ic exhibit signals at high field, a singlet (2 H) at 0·65 and a signal (1 H) superimposed on the methyl peaks appear to be indicative of a cyclopropane ring.

In the NMR spectrum of dihydrozaluzanin A diacetate (IIIc) the low field doublets of the exocyclic methylene group of Ic are not observed. A doublet centered at 1·40 corresponds to a new secondary methyl group.

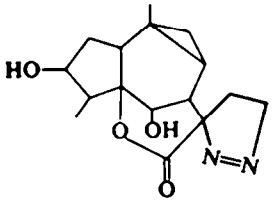
[1] Contribution No. 230 from the Instituto de Química de la Universidad Nacional Autónoma de México.
[2] The NMR spectra by Mr. Eduardo Díaz, on a Varian A-60 spectrometer in $CDCl_3$ soln, using TMS as internal reference. All chemical shifts are reported in ppm as δ values (c/s/60).
[3] W. Herz, H. Watanabe, M. Miyasaki and Y. Kishida, *J. Amer. Chem. Soc.* **84**, 2601 (1962).

Alkaline treatment of zaluzanin A (Ia) gives an isomeric product, allozaluzanin A (IVa) (λ max 207 mμ; ϵ 13640). Its IR spectrum shows bands at 1775 and 1665 cm^{-1}, corresponding to an α,β-unsaturated five membered lactone. Allozaluzanin A (IVa) formed under basic acetylation conditions a monoacetate (IVb) which still shows an hydroxyl IR band at 3600 cm^{-1}. The NMR spectrum of IVb exhibits two doublets at 6·13 and 5·72 [J = 1 c/s) of the exocyclic methylene protons, the hydrogen on the carbon bearing the acetoxy group is responsible for a triplet [J = 9 c/s) centered at 5·12. The lactone is closed to a secondary hydroxyl group as shown by a doublet [J = 7 c/s) centered at 4·11. A singlet at 2·96, assigned to the tertiary hydroxyl group disappears on equilibration with deuterium oxide. In the methyl region, the acetyl group shows a singlet at 2·07. A singlet at 1·03 superimposed on a doublet (J = 7 c/s) corresponds to a tertiary and a secondary methyl group, respectively. The chemical shift of a signal (1 H) superimposed on the methyl peaks and a multiplet (2 H) at 0·41, is new evidence of the presence of a cyclopropane ring.

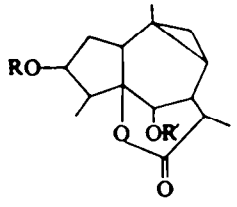


I

a, R = R′ = H
b, R = Ac R′ = H
c, R = R′ = Ac



II



III

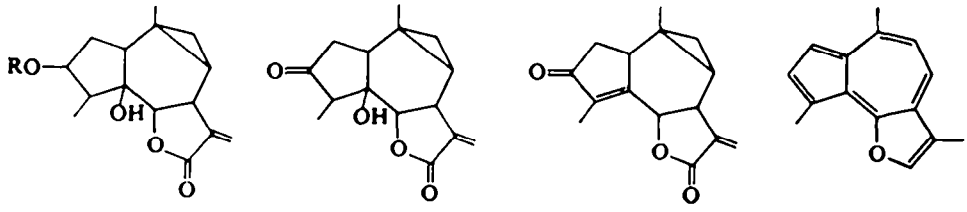
a, R = R′ = H
b, R = Ac; R′ = H
c, R = R′ = Ac

Chromium trioxide oxidizes the secondary hydroxyl group of allozaluzanin A (IVa) to a 5-membered ketone, the resulting dehydroderivative (V) shows in the IR spectrum a broad band with two peaks at 1770 cm^{-1} (γ-lactone) and at 1745 cm,^{1} (cyclopentanone). In the NMR spectrum of V are a pair of low field doublets (J = 1 c/s) at 6·25 and 5·87 (exocyclic methylene). A doublet at 4·33 (J = 6 c/s) (C-6 hydrogen) spin coupled with a triplet centered at 3·5 (J = 6 c/s) (allylic proton), the latter superimposed with a sharp singlet which disappears on equilibration with deuterium oxide (hydroxyl proton). A doublet centered at 1·20 (J = 7 c/s) and a singlet at 1·10 (C-7 and C-10 methyl groups, respectively). A signal (1 H) superimposed on the methyl peaks and a singlet (2 H) at 0·59 (cyclopropane protons). The relative position of the tertiary hydroxyl group of IVa was established by dehydration of dehydroallozaluzanin A (V) with *p*-toluenesulfonic acid to the anhydroderivative (VI), (λ_{max} 213 and 233 mμ; ϵ 13688, 16600). It has IR bands at 1770 cm^{-1} (γ-lactone) and at 1705 cm^{-1} (cyclopentenone).

The features of the NMR spectrum of VI correspond to a sesquiterpene lactone closed to C-6 of the guaiane series with a C-3 keto grouping. The exocyclic methylene protons show two low field doublets (J = 2 c/s) at 6·32 and 5·82. The C-7 allylic hydrogen shows a multiplet at 3·24 and a signal at 2·5 (3 H) is ascribed to the protons at C-1 and C-2. The vinyl methyl group exhibits a triplet at 1·87 (J = 1·5 c/s) indicating homoallylic coupling with H_1 and also with H_6, confirmed by the multiplicity of the signal of the C-6 proton. The latter shows a pair of quadruplets centered at

5·37 ($J_{H_6-H_7}$ = 7 c/s) with a long range coupling of 1·5 c/s.[4] The cyclopropane moiety formed by a linkage between C-8 and C-10 is responsible for a singlet (3 H) at 0·90 (C-10 methyl group) and a multiplet (3 H), partially superimposed on the singlet, centered at 0·80.

The guaiane skeleton of zaluzanin A (Ia) was established by Pd–C dehydrogenation of the crude product obtained after LAH reduction of IIIa. This reaction results in formation of artemazulene (VII) and chamazulene (VIII), characterized as their TNB adducts. The formation of artemazulene (VII) proves the presence of a C-6 hydroxyl group in zaluzanin A (Ia). Therefore the alkaline treatment of Ia isomerizes the 6-membered lactone closed at C-5 to the γ-lactone oriented at C-6 in allozaluzanin A (IVa).



IV V VI VII

a, R = H
b, R = Ac

The C-6 hydroxyl group of zaluzanin A (Ia) is relatively hindered since it is not oxidized by mild treatment with chromium trioxide. Dehydrozaluzanin A (IX) (λ_{max} 210 mμ; ϵ 7310) has IR bands at 3640 and at 3420 cm^{-1} (hydroxyl group) and a broad band with two peaks at 1750 and 1725 cm^{-1} (cyclopentanone and six-membered lactone). The NMR spectrum of IX exhibits a pair of low field doublets at 6·13 and 5·60 (J = 1 c/s) corresponding to the exocyclic methylene. A doublet at 3·37 (J = 4 c/s) of the hydroxyl proton disappears on equilibration with deuterium oxide. A triplet (J = 3 c/s) centered at 4·00 ascribed to the C-6 hydrogen collapses after the above treatment to a doublet (J = 2 c/s) spin coupled to a similar signal ascribed to the C-7 allylic hydrogen. A singlet at 1·06 and a doublet (J = 7 c/s) at 1·01 partially superimposed on the singlet are assigned to the C-10 and C-4 methyl groups, respectively. A signal (1 H) partially superimposed on the methyl peaks and a singlet (2 H) at 0·70 correspond to the cyclopropane protons.

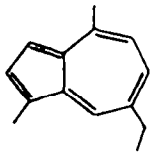
Chromium trioxide oxidation of dihydrodehydrozaluzanin A (X) obtained by Pd–C catalyzed hydrogenation of IX yields bisdehydrodihydrozaluzanin A (XI). Its IR spectrum shows a broad band at 1740 cm^{-1} of the combined carbonyl functions. In the NMR spectrum of XI, the C-10 methyl group is responsible for a singlet at 1·15, two doublets (J = 7 c/s), centered at 1·48 and at 1·06 correspond to the secondary methyl groups at C-11 and C-4. Two signals (intensity 1 proton each) superimposed on the methyl peaks and a triplet (J = 5 c/s) centered at 0·47 are assigned to the hydrogens of the cyclopropane ring.

Hydrochloric acid treatment of XI in ethanol affords an optically inactive product whose structure (XII) is based on spectroscopic features. The IR spectrum of XII exhibits bands at 1750 cm^{-1} (($\alpha.\beta$-unsaturated 5-membered enol lactone), at 1690 cm^{-1}

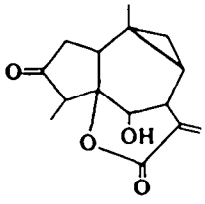
[4] J. T. Pinhey, *Tetrahedron Letters* No. 4, 271 (1963).

(cyclopentenone), at 1640 and 1615 cm^{-1} (C=C double bonds). It shows UV max at 202, 244, 332 and 349 mμ; (ϵ 5713, 6784, 32400, 7837). In the NMR spectrum, the vinyl proton is responsible for a singlet at 6·11, a doublet [J = 7 c/s), centered at 3·20 corresponds to the proton at C-4 a complex signal (3 H) centered at 2·83 is assigned to the allylic hydrogens at C-8 and C-10. The vinyl methyl group is responsible for a singlet at 1·89, partially superimposed on a broad signal (2 H), ascribed to the protons at C-9. Two superimposed doublets (J = 7 c/s) centered at 1·32 corresponds to the secondary methyl groups.

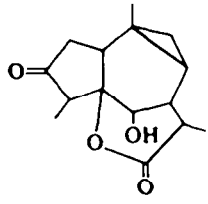
On alkaline treatment, dihydrozaluzanin A (IIIa) yields dihydroallozaluzanin A (XIIIa), whereas hydrogenation of allozaluzanin A (IVa) affords the C-11 epimeric dihydroderivative (XIIIb). Chromium trioxide oxidation of XIIIa gives the dihydrodehydroderivative (XIV).



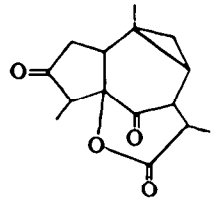
VIII



IX



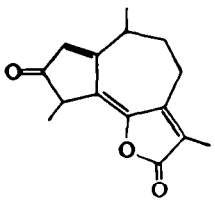
X



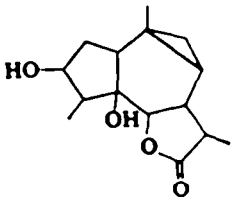
XI

Zaluzanin B, $C_{17}H_{22}O_5$, m.p. 223–225°, $[\alpha]_D$ −12 (λ_{max} 209 mμ; ϵ 8109); is eluted in the less polar fractions of the chromatogram. It has IR bands at 3620 and 3440 cm^{-1} (hydroxyl bands), at 1710 cm^{-1} (acetyl group and 6-membered lactone), at 1640 cm^{-1} (C=C double bond). The NMR spectrum suggests that zaluzanin B (Ib) is a C-3 acetyl derivative of zaluzanin A (Ia). A pair of two low field doublets at 6·10 and 5·53 (J = 1 c/s) correspond to the exocyclic methylene protons. The multiplicity of a signal centered at 5·26 indicates that the proton on the carbon carrying the acetoxy group is at C-3. A doublet at 3·16 (J = 2 c/s) is attributed to the allylic hydrogen at C-7. The hydroxyl proton is responsible for a doublet at 3·56 (J = 4 c/s). On equilibration with deuterium oxide this doublet disappears and a signal centered at 3·90 ascribed to the C-6 hydrogen is clearly observed as a doublet (J = 2 c/s) spin coupled with H_7. In the methyl region the singlets at 2·08, 1·04 and a doublet (J = 7 c/s), centered at 0·88 are assigned to the acetyl group and to the methyl groups at C-10 and C-4, respectively. A signal (1 H) superimposed on the methyl peaks and a singlet (2 H) at 0·58 are ascribed to the protons of the cyclopropane ring.

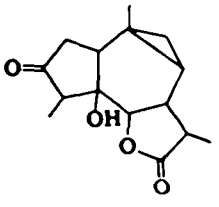
Hydrogenation of zaluzanin B (Ib) affords the dihydroderivative (IIIb) identified with dihydrozaluzanin A acetate obtained by controlled acetylation of IIIa. Chromium trioxide oxydation of IIIb yields dihydrodehydrozaluzanin B (XV).



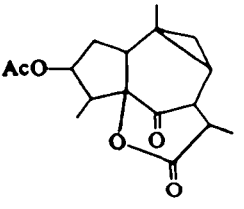
XII



XIII



XIV



XV

Zaluzanin A (Ia) appears to have a *trans* ring junction at C-1 (α-H) and C-5 as shown by the Cotton effects displayed by the ORD curves of the dehydroderivatives (V and IX) which are very similar in sign and amplitude to the strong negative Cotton effects of the 16-ketosteroids.[5] Furthermore, biogenetic considerations suggest that the C-7 side chain possesses a β-configuration. Therefore, the C-5 hydroxyl group of zaluzanin A (Ia) involved in the 6-membered lactone is also β-oriented. The long range coupling of the C-6 hydrogen exhibited by the NMR spectrum of VI (*vide supra*) indicates that it possesses a β-configuration,[4] the C-6 hydroxyl group being α-oriented.

EXPERIMENTAL[6]

Isolation of zaluzanins A and B. Zaluzania augusta[7] dried and ground (except the roots) (1 Kg) was extracted twice with EtOH (6 l.) under reflux for 20 hr. The combined extracts were concentrated to 2 l. treated with a soln of lead acetate (20 g) in water (2 l.), left at room temp for 2 hr. filtered, diluted with water (2 l.) and extracted with chf. The extract was evaporated to dryness, the residue dissolved in benzene and chromatographed on alumina. Zaluzanin B (1b) crystallized in the fractions eluted with benzene. Recrystallization from acetone–ether afforded needles (200 mg), m.p. 223–225°, $[\alpha]_D$ −12°: UV: 209 mμ: ε, 8109. IR: 3620 and 3440 (OH group), 1710 (Ac group and 6-membered lactone) and 1640 cm^{-1} (C—C double bond). (Found: C, 67·20; H, 7·20; O, 25·88. Calc. for $C_{17}H_{28}O_6$: C, 67·65; H, 7·24; O, 26·11%.)

The polar fractions eluted with ether and increasing proportions of chf and with AcOEt gave semicrystalline residues. These fractions were combined and recrystallized from acetone–ether yielding Ia (1·2 g) m.p. 256–258°. Further crystallizations from MeOH raised the m.p. to 265°, $[\alpha]_D$ −10° (EtOH), UV: 210 mμ; ε, 9815; IR (KBr): at 3400 (OH) groups 1695 and 1638 cm^{-1} (α,β-unsaturated 6-membered lactone). (Found: C, 68·43; H, 7·55; O, 23·82. Calc. for $C_{15}H_{20}O_4$: C, 68·16; H, 7·63; O, 24·21%.)

Pyrazoline of zaluzanin A (II). A soln of Ia (100 mg) in MeOH (2 ml) was treated with an ethereal soln of diazomethane, and allowed to stand at 4° overnight and evaporated to dryness *in vacuo* at room temp. Crystallization of the residue from acetone–ether yielded prisms m.p. 158–160° (dec); $[\alpha]_D$ −327°; (diox); UV: 332 mμ; ε, 160; IR: 3610 and 3410 (OH groups), 1725 cm^{-1} (6-membered lactone). (Found: C, 62·70; H, 7·03; O, 21·15; N, 9·10. Calc. for $C_{16}H_{22}O_4N_2$: C, 62·72; H, 7·24; O, 20·89; N, 9·14%.)

Zaluzanin A diacetate (Ic). Acetylation of Ia with pyridine–Ac_2O for 3 hr on the steam bath afforded Ic, m.p. 108–109° (needles from ether–hexane); $[\alpha]_D$ −22°; UV: 208 mμ; ε, 10114; IR: 1720 (Ac group and 6-membered lactone) and 1645 cm^{-1} (C—C double bond). (Found: C, 65·73; H, 7·11; O, 27·66. Calc. for $C_{19}H_{24}O_6$: C, 65·50; H, 6·94; O, 27·65%.)

Dihydrozaluzanin A (IIIa). A soln of Ia (250 mg) in MeOH (40 ml) with 10% Pd–C (80 mg) was hydrogenated until the uptake of H ceased, the catalyst was filtered off and the soln concentrated, by addition of ether, IIIa crystallized as needles (240 mg), m.p. 260°, $[\alpha]_D$ +50·5° (EtOH), IR (KBr): 3340 (OH groups) and 1700 cm^{-1} (6-membered lactone). (Found: C, 67·47; H, 8·25; O, 24·23. Calc. for $C_{15}H_{22}O_4$: C, 67·64; H, 8·33; O, 24·03%.)

Hydrogenation of Ia (400 mg) in MeOH soln with RuO_2 at 70° and 1000 lb/psi for 16 hr afforded IIIa, (320 mg) m.p. 250–252°.

Dihydrozaluzanin A 3-monoacetate (IIIb). A soln of IIIa (425 mg) in AcOH (15 ml) was treated with 3 drops 62% $HClO_4$ and left at room temp for 20 hr, poured in ice water and extracted with AcOEt. The organic layer was washed with 5% NaOHaq and water, dried (Na_2SO_4) and evaporated to dryness. Crystallization from acetone–ether gave 40 mg of recovered IIIa, m.p. 250–252°. From

[5] C. Djerassi, R. Riniker and B. Riniker, *J. Amer. Chem. Soc.* **78**, 6362 (1956).

[6] M.p's are uncorrected. Analyses by Dr. F. Pascher, Bonn, Germany. UV spectra: 95% EtOH soln, Beckman DK2 spectrophotometer. IR spectra: $CHCl_3$ soln, Perkin–Elmer 21 double beam spectrophotometer. Rotations in chf at 20° unless noted otherwise.

[7] We are grateful to Dr. Arturo Gómez Pompa of the Instituto de Biología (U.N.A.M.) for the classification of the plant. Voucher Number Romo No. 1. Herbario Nacional de la UNAM (MEXU).

the mother liquors, IIIb (160 mg), m.p. 205–211° was obtained. Several crystallizations from acetone–ether raised the m.p. to 228–231°, $[\alpha]_D$ +24°; IR: 3620 (OH group) and 1720 cm^{-1} (broad, Ac group and 6-membered lactone). (Found: C, 66·01; H, 7·96; O, 26·16. Calc. for $C_{17}H_{24}O_6$: C, 66·21; H, 7·84; O, 25·95%.)

Dihydrozaluzanin A diacetate (IIIc). Acetylation of IIIa with pyridine–Ac_2O for 1 hr on the steam bath furnished the IIIc, m.p. 162–164° (prisms from ether–pentane), $[\alpha]_D$ +40·5°; IR: 1725 cm^{-1} (broad, Ac groups and 6-membered lactone). (Found: C, 65·14; H, 7·21; O, 27·37. Calc. for $C_{19}H_{26}O_6$: C, 65·12; H, 7·48; O, 27·40%.)

Allozaluzanin A (IVa). Compd Ia (2 g) was dissolved in MeOH (15 ml), treated with KOH (2 g) in 40 ml water and refluxed for 40 min. cooled, acidified with dil HCl and extracted with AcOEt. The organic soln was washed with water, dried (Na_2SO_4) and evaporated to dryness. Crystallization of the residue from acetone–hexane yielded 730 mg, m.p. 191–194°. Further crystallizations from acetone–hexane raised the m.p. to 196–197°, $[\alpha]_D$ −121°, UV: 207 mμ; ϵ, 13640; IR: 3600 (OH group), 1775 and 1668 cm^{-1} (α,β-unsaturated γ-lactone). (Found: C, 68·22; H, 7·63; O, 24·06. Calcd. for $C_{15}H_{20}O_4$: C, 68·16; H, 7·63; O, 24·21%.)

Allozaluzanin A acetate (IVb). Acetylation of IVa with Ac_2O–pyridine for 2 hr on the steam bath yielded IVb, m.p. 138°; $[\alpha]_D$ −143°; UV: 211 mμ; ϵ, 8500; IR: 3600 (OH band), 1770, 1668 (α,β-unsaturated γ-lactone) and 1725 cm^{-1} (Ac group). (Found: C, 66·66; H, 7·20; O, 26·30. Calc. for $C_{17}H_{22}O_5$: C, 66·56; H, 7·24; O, 26·11%.)

Dehydroallozaluzanin A (V). A soln of IVa (250 mg) in acetone (20 ml) was treated with 8N CrO_3[6] at 5° until the persistence of an orange colour. The soln was diluted with AcOEt, washed with water, dried and evaporated to dryness. Crystallization of the residue from acetone–hexane yielded needles (175 mg), m.p. 180–182°; $[\alpha]_D$ −290·5°; UV: 207 mμ; ϵ, 14529; IR: 3600 and 3475 (OH group) a broad band with 2 peaks at 1770 and 1745 (cyclopentanone and γ-lactone), 1662 cm^{-1} (C=C double bond). RD (dioxan); $[\alpha]_{600}$ −794°, $[\alpha]_{360}$ −1228°, $[\alpha]_{330}$ −2180°, $[\alpha]_{315}$ −3712°, $[\alpha]_{310}$ −3410°. (Found: C, 68·64; H, 6·82; O, 24·56. Calc, for $C_{15}H_{18}O_4$: C, 68·68; H, 6·92; O, 24·40%.)

Dehydroanhydroallozaluzanin A (VI). A soln of V (150 mg) and *p*-toluenesulfonic acid (40 mg) in EtOH (10 ml) was heated under reflux for 20 min, concentrated to $\frac{1}{2}$ vol, diluted with water and extracted with AcOEt. The organic layer was washed with $NaHCO_3$aq, dried and evaporated to dryness. Crystallization from acetone–hexane yielded prisms m.p. 134°, $[\alpha]_D$ −18°; UV: 213, 233 mμ; ϵ, 13688, 16600; IR: 1770 (γ-lactone), 1705 (cyclopentenone) and 1660 cm^{-1} (C=C double bond). (Found: C, 73·65; H, 6.54; O, 19·96. Calc. for $C_{15}H_{16}O_3$: C, 73·75; H, 6·60; O, 19·65%.

Aromatization of dihydrozaluzanin A (IIIa). A soln of IIIa (720 mg) in THF (100 ml) was treated with LAH (2 g) and heated under reflux for 10 hr. The excess of LAH was decomposed with AcOEt and water. The ppt was filtered and the soln evaporated to dryness. The oily residue (650 mg) was treated with Nujol (15 ml) and 10% Pd–C (2 g) was added. The mixture was heated to 310° for 20 min, cooled, diluted with hexane and extracted with 86% H_3PO_4. The azulene complex was decomposed with ice water and the azulenes extracted with hexane. Compounds VIII and VII were separated by chromatography on alumina and converted to their TNB adducts. Crystallization of VIII from MeOH afforded dark brown needles (15 mg), m.p. 127–129°. The VII adduct yielded black needles (30 mg), m.p. 176–182° further crystallizations from MeOH raised the m.p. to 190–191°. Both adducts were identified by the standard methods with authentic samples.

Alkaline treatment of dihydrozaluzanin A (IIIa). A soln of IIIa (400 mg) in MeOH was treated with KOH (400 mg) in water (2 ml), heated under reflux for 40 min diluted with water, acidified with dil HCl and extracted with AcOEt. The organic solution was washed with water, dried and evaporated to dryness. Crystallization of the residue from acetone–ether yielded XIIIa (260 mg), as prisms, m.p. 238–240°, $[\alpha]_D$ −57°; IR: 3570 (OH groups) and 1780 cm^{-1} (γ-lactone). (Found: C, 67·87; H, 8·16; O, 23·96. Calc. for $C_{15}H_{22}O_4$: C, 67·64; H, 8·33; O, 24·03%.)

Dehydrodihydroallozaluzanin A (XIV). An acetone soln of XIII (180 mg) was oxidized with 8N CrO_3. Crystallization from acetone–ether yielded prisms m.p. 215°, $[\alpha]_D$ −192°; IR: 3595 and 3460 (OH group), 1775 (γ-lactone) and 1772 cm^{-1} (cyclopentanone). (Found: C, 68·25; H, 7·76; O, 24·40. Calc. for $C_{15}H_{20}O_4$: C, 68·16; H, 7·63; O, 24·21%.)

Hydrogenation of allozaluzanin A (IVa). A soln of IVa (100 mg) in AcOEt (20 ml) was hydrogenated with 40 mg of 10% Pd–C until the uptake of H ceased. The soln was filtered and evaporated to

[6] A. Bowers, T. G. Halsall, E. R. H. Jones, A. J. Lemin, *J. Chem. Soc.* 2548 (1953).

dryness. Crystallization of the residue from acetone–hexane afforded XIIIb (40 mg), m.p. 205°; IR: 3580 (OH groups) and 1780 cm^{-1} (γ-lactone). (Found: C, 67·47; H, 8·43; O, 24·48. Calc. for: $C_{16}H_{22}O_4$: C, 67·64; H, 8·33; O, 24·03%.)

Dehydrozaluzanin A (IX). A soln of Ia (1·5 g) in acetone (120 ml) at 5° was oxidized with 8N CrO_3 until the persistence of an orange colour, the soln was immediately diluted with AcOEt and washed with water and $NaHCO_3$aq, dried and evaporated. Crystallization from acetone–ether afforded prisms (980 mg), m.p. 178°; $[\alpha]_D$ −171°; UV: 210 mμ; ϵ, 7310; IR: 3640 and 3420 (OH group), a broad band with 2 peaks at 1750 and 1725 (cyclopentanone and 6-membered lactone), and 1650 cm^{-1} (C=C double bond) RD (dioxan); $[\alpha]_{600}$ - 556°, $[\alpha]_{546}$ −967°, $[\alpha]_{330}$ 2222°, $[\alpha]_{317}$ - 4366°, $[\alpha]_{316}$ - 4190°. (Found: C, 68·60; H, 6·82; O, 24·68. Calc. for $C_{15}H_{18}O_4$: C, 68·68; H, 6·92; O, 24·40%.)

Ozonolysis of dehydrozaluzanin A (IX). A soln of the lactone (300 mg) in AcOEt (25 ml) was ozonized for 15 min at −70°, hydrogenated then with 10% Pd–C (50 mg) until the uptake of H ceased, filtered and distilled into an AcOEt soln of dimedone (40 mg). This soln was evaporated to dryness and the residue crystallized from MeOHaq yielding 15 mg of formaldehyde-dimedone m.p. 186–189° identified with an authentic sample by the standard methods.

Dihydrodehidrozaluzanin A (X). Hydrogenation of IX (980 mg) in AcOEt (80 ml) with 10% Pd–C (100 mg) until the uptake of H ceased, furnished X (920 mg), m.p. 175–177° (needles from acetone–hexane), $[\alpha]_D$ - 166°; IR: 3620 and 3465 (OH group) and 1740 cm^{-1} (broad, cyclopentanone and 6-membered lactone). (Found: C, 68·23; H, 7·42; O, 24·34. Calc. for $C_{15}H_{20}O_4$: C, 68·16 H, 7·63; O, 24·21%.)

Bisdehydrodihydrozaluzanin A (XI). An acetone soln of X (920 mg) was oxidized with 8N CrO_3. Crystallization from acetone–hexane furnished prisms (700 mg), m.p. 158–159·5°; $[\alpha]_D$ 171°; UV: 208, 288 mμ; ϵ, 738, 40; IR: 1740 cm^{-1} (broad, cyclopentanone, cyclohexanone and 6-membered lactone). (Found: C, 68·61; H, 6·89; O, 24·76. Calc. for $C_{15}H_{18}O_4$: C, 68·68; H, 6·92; O, 24·40%.)

HCl *treatment of bisdehydrodihydrozaluzanin A* (XI). A soln of XI (700 mg) in EtOH (25 ml) with conc. HCl (2 ml) was heated under reflux for 1 hr, diluted with water, and the oily ppt extracted with AcOEt. The organic layer was washed with water, $NaHCO_3$aq, dried and evaporated to dryness. The residue (520 mg) was chromatographed on alumina (10 g). The crystalline fractions eluted with benzene–hexane 1:4 and 1:3 were combined and recrystallized from hexane yielding XII as yellow prisms (60 mg), m.p. 100–103°, $[\alpha]_D$ ±0; UV: 202, 244, 332 and 349 mμ; ϵ, 5713, 6784, 32400 and 7837; IR: 1750 (γ-lactone), 1690 (cyclopentenone), and 1640, 1615 cm^{-1} (C=C double bonds). (Found: C, 73·55; H, 6·45; O, 19·60. Calc. for $C_{15}H_{16}O_3$: C, 73·75; H, 6·60; O, 19·65%.)

Dihydrozaluzanin B (IIIb). A soln of Ib (90 mg) in MeOH (20 ml) was hydrogenated with Pd–C (20 mg) until the uptake of H ceased. The catalyst was filtered off and the soln evaporated to dryness. Crystallization from acetone–ether afforded (55 mg) m.p. 233–235°. Mixed m.p. with IIIb was undepressed and the IR spectra were superimposable.

Acetylation of IIIb with Ac_2O–pyridine afforded IIIc, m.p. 162–165°, identified by the standard methods with dihydrozaluzanin A diacetate.

Dihydrodehydrozaluzanin B (XV). CrO_3 oxidation of an acetone solution of IIIb (40 mg) yielded 25 mg of XV, needles from acetone–hexane, m.p. 109°, IR: 1730 cm^{-1} (broad, Ac group, cyclohexanone and 6-membered lactone). (Found: C, 66·46: H, 7·18; O, 25·98. Calc. for $C_{17}H_{18}O_4$: C, 66·65; H, 7·24; O, 26·11%.)