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The Structure and the Stereochemistry of Solidagonic Acid

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A new bitter principle, solidagonic acid $C_{22}H_{34}O_4$, was isolated from the root of *Solidago altissima* L. It is a bicyclic diterpene carboxylic acid, having an acetoxyl group and two double bonds, and was formulated as II on the basis of chemical and spectroscopic studies. The other constituents of the root, kolavenic acid (XXIV) and kolavenol (XXVIII) were also isolated, and they were chemically correlated to II. The absolute configurations of II, XXIV and XXVIII were established by application of the octant rule on the ORD curves for some ketonic compounds derived from them.

We have previously reported[1] the isolation and structual elucidation of solidagonic acid, a bitter principle isolated from the root of *Solidago altissima* L. We now present evidences in full detail about its constitution and stereochemistry.

S. altissima L. (Compositae) is a perennial plant native to North America, and now grows all over Japan. Its root has a considerable bitter taste. Several investigations have been reported about the constituents of Solidago species,[2-4] and recently, a diterpene ketone, named solidagenone, was isolated from the root of *S. canadensis* L. and *S. giganitia*. Its structure was deduced as I from spectroscopic and chemical studies.[5] However, nothing has been reported about a bitter principle, and thus our study was undertaken.

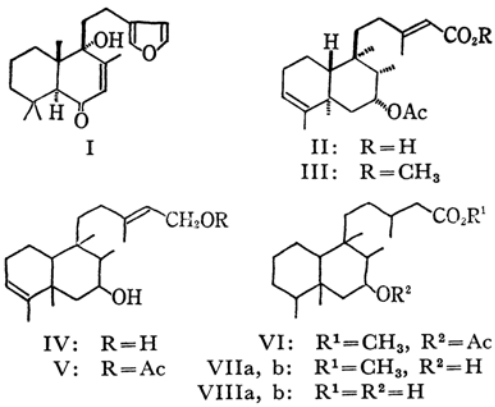


Fig. 1

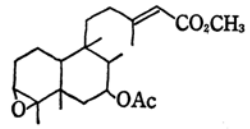
Results and Discussion

An ethanol extract of the root of *S. altissima* L. was chromatographed repeatedly on silica-gel and silicic acid columns, and a bitter principle was isolated. It was a carboxylic acid and named solidagonic acid (II), $C_{22}H_{34}O_4$, mp 143—144°C, $[\alpha]_D^{12}$ −97.6°. Compound II was treated with diazomethane to give the methyl ester (III) $C_{23}H_{36}O_4$, mp 106.5°C, $[\alpha]_D^{12}$ −98.8°. Later, the method of isolation was improved and III was isolated from the dried root in about a 0.3% yield.

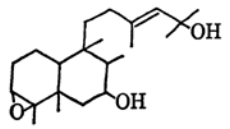
The IR spectrum of II indicated the presence of an ester (ν_{max}^{KBr} 1732, 1237 cm^{-1}) and an α,β-unsaturated acid (3400—2400, 1680, 1637 cm^{-1}). The UV spectra of II and III also suggested the presence of α,β-unsaturated acid (λ_{max}^{EtOH} 217.5 mμ ε 9090) and ester function (217.5 mμ, ε 15400), respectively. The NMR spectrum of II showed the presence of a carboxylic acid (δ 11.75, 1H), an acetyl group (2.00, 3H s), two tertiary methyl groups (0.97 and 1.17, each 3H s), one secondary methyl group (0.92, 3H d J=7 cps) and two olefinic methyl groups (1.59 and 2.18, each 3H slightly splitting singlet). Among them a signal at 2.18 ppm predicted the presence of the $-C(CH_3)=\overset{|}{C}-CO_2H$ group and this was supported by the fact that the signal shifted to 1.65 ppm upon converting III to the diol (IV) by lithium aluminum hydride reduction.

Compound III absorbed 2 mol of hydrogen on catalytic hydrogenation and gave the tetrahydro methyl ester (VI), which proved to be a mixture of stereosiomers (see below). Its NMR spectrum showed the presence of one hydrogen on the carbon atom bearing the acetoxyl group (δ 4.97, 1H broad). Furthermore, calculation of the degree of unsaturation concluded that III has a bicyclic

1) S. Kusumoto, T. Okazaki, A. Ohsuka and M. Kotake, *Tetrahedron Letters*, **1968**, 4325.
2) E. Wada, *Kagaku (Science)*, **22**, 217 (1952).
3) L. Skrzypczakowa, *Acta Polon. Pharm.*, **18**, 39 (1961).
4) K. Stavholt Baalsrud, D. Holme, M. Nestvolt, J. Pliva, J. Stene Sörensen and N. A. Sörensen, *Acta Chem. Scand.*, **6**, 883 (1952).
5) T. Anthonsen, P. H. McCabe, R. McCrindle and R. D. H. Murray, *ibid.*, **21**, 2289 (1967).



IX



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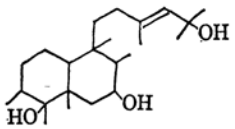

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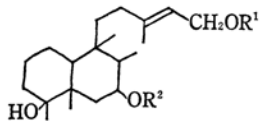
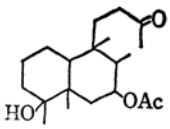
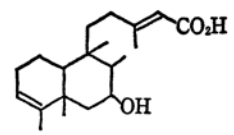


XII: $R^1=R^2=H$
XIII: $R^1=Ac$, $R^2=H$
XIV: $R^1=R^2=Ac$

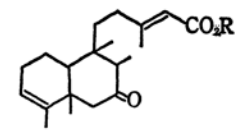


XV

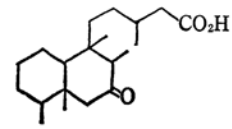
Fig. 2



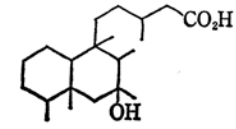
XVI



XVII: R=H
XVIII: R=CH_3



XIX



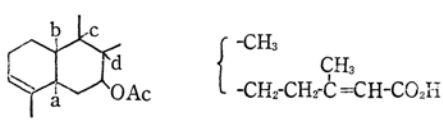
XX

Fig. 3

structure. The carbon skeleton of II is a decaline type since III gave 1,2,5-trimethylnaphthalene when dehydrogenated on selenium or palladium-charcoal.

When III was oxidized with one mole of monoperphthalic acid, a single monoepoxide (IX) $C_{23}H_{36}O_5$, mp 135.5—136.5°C, was obtained. It is clear from the IR and NMR spectra that the terminal α,β-unsaturated ester function remained unchanged (ν_{max}^{KBr} 1715, 1640 cm^{-1}; δ 2.41 3H d J=1.1 cps, and 5.53 1H broad singlet), and the other double bond was epoxidized (δ 1.15 3H s, and 2.77 1H triplet like). After introducing a methyl group into the epoxide ring, the product (XI) was dehydrogenated to afford 1,2,5,6-tetramethylnaphthalene, mp 116—117°C. Hence, one of the double bonds in II was fixed at C-3. The monoepoxide (IX) was reduced with lithium aluminum hydride to give the triol (XII) $C_{20}H_{36}O_3$, mp 120—121.5°C. When XII was acetylated with acetic anhydride and pyridine at room temperature, a monoacetate (XIII) $C_{22}H_{38}O_4$, mp 142.5—143.5°C, was obtained. This monoacetate was further acetylated at 100°C to afford an oily diacetate (XIV) (ν_{max}^{Oil} 3500 cm^{-1}; δ 1.97 6H s). Ozonolysis of XIV gave a methyl ketone (XV) $C_{20}H_{34}O_4$, mp 104—105°C, (ν_{max}^{KBr} 1705 cm^{-1}; δ 2.10 3H s). Thus, the structure of another double bond in II was confirmed as $-C(CH_3)=CHCO_2H$

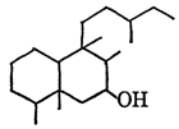
An attempt to establish the position of the acetoxyl group in II was then undertaken. Compound III was hydrolyzed with methanolic potassium hydroxide and the resultant hydroxy acid (XVI), which could not be crystallized, was oxidized with Jones reagent to furnish the keto acid (XVII) which also could not be crystallized. Therefore, XVII was esterified with diazomethane and the product was purified on a silica-gel column to give an oily keto ester (XVIII), which was chracterized as the 2,4-dinitrophenylhydrazone $C_{27}H_{36}O_6N_4$, mp 174°C. When the keto ester (XVIII) was treated with methyl magnesium bromide, an expected product could not be isolated in a satisfactory yield, probably due to further reactions initiated by the ready dehydration of the terminal allylic tertiary alcohol. Thus, this sequence of the reactions was carried out with the tetrahydro series of compounds in the following manner. A crystalline tetrahydro hydroxy acid was obtained by hydrolysis of the tetrahydro derivative (VI) mentioned above, but the yield was poor and a considerable amount of an oil, which could not be crystallized, was obtained from the mother liquor. Therefore, the product of hydrolysis was esterified with diazomethane and two methyl esters were isolated by repeated chromatography on a silica-gel column: VIIa an oil; and VIIb $C_{21}H_{38}O_3$, mp 84—87°C. These esters were hydrolyzed to the corresponding two tetrahydro hydroxy acids: VIIIa $C_{20}H_{36}O_3$, mp 99—100°C; VIIIb $C_{20}H_{36}O_3$, mp 142—144°C. Since the IR spectra of these two acids in chloroform were almost identical, they are considered to be the stereoisomers formed by catalytic hydrogenation. The hydroxy acid (VIIIb) was oxidized with Jones reagent to the keto acid (XIX) $C_{20}H_{34}O_3$, mp 82—83°C. The position of the ketone was marked with methyl Grignard reagent, and the resultant hydroxy acid (XX) was dehydrogenated on selenium to give 1,2,3,5-tetramethylnaphthalene.[6] Thus, the position of acetoxyl group in II was unequivocally defined at C-7.



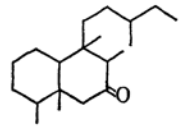
XXI

Fig. 4

6) D. E. A. Rivett, *J. Chem. Soc., (C)*, **1966**, 1892.



XXII

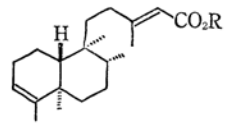


XXIII

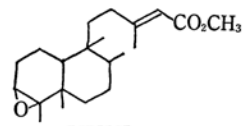
Fig. 5

The structure of solidagonic acid (II) proposed on the basis of the foregoing results should have the partial structure represented by XXI, in which the remaining tertiary methyl group and the side chain must be attached to some of the four possible positions *a*—*d*. The positions of the remaining tertiary substituents and the secondary methyl group were determined as follows. The diol (IV) gave the 7-monoalcohol (XXII) on hydrogenation over Adams catalyst in acetic acid - ethanol accompanied with hydrogenolysis of the terminal allylic alcohol. Oxidation of XXII with Jones reagent furnished the 7-ketone (XXIII) $C_{20}H_{36}O$, bp 125—133°C (bath)/1mmHg. The NMR spectrum of XXIII showed the presence of only three hydrogens adjacent to carbonyl group in the region of δ 1.8—2.7 ppm (δ 2.45 1H q J=6.7 cps, δ 1.94 and 2.28 AB type each 1H d J=12 cps). The former was assigned to the hydrogen at C-8 which coupled only with the three hydrogen atoms in the C-8 methyl group. The latter two were assigned to the C-6 methylene protons which coupled only with each other. Consequently the secondary methyl group was fixed at C-8, and it is clear that C-5 and C-9 carry no hydrogen. Although it is not possible to confirm the nature of the remaining two residues attached to C-5 and C-9, the structure represented by II is the most probable one, as judged from the NMR spectra of the two tertiary methyl groups of the various derivatives prepared (see below). Moreover, this structure is the so-called "rearranged labdane skeleton" of the type exhibited by the cascarillins,[7] and it is also reasonably explained on the basis of biogenetic considerations.[8-10] Therefore, the constitution of solidagonic acid is deduced as II.

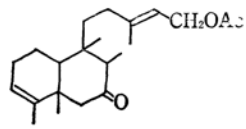
Kolavenic acid (XXIV) was isolated from a benzene extract of the dried root as its methyl ester (XXV) $C_{21}H_{34}O_2$, bp 151—152°C/1 mmHg, $[\alpha]_D^{26}$ −60.8°. Its IR spectrum suggested the presence of an α,β-unsaturated ester group and its NMR spectrum showed the presence of two tertiary methyl groups (δ 0.76 and 1.02 each 3H s), one



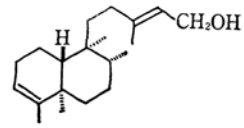
XXIV: R=H
XXV: R=CH3



XXVI



XXVII



XXVIII

Fig. 6

secondary methyl group (0.85 3H d J=6 cps)' two olefinic methyl groups (1.60 and 2.18 each 3H) and two olefinic protons (5.15 1H m, and 5.59 1H broad singlet). The terminal $-C(CH_3)=CH-CO_2H$ group was also expected in XXIV by comparison of these spectra with those of II and III. The compound XXIV was assigned to desacetoxyl solidagonic acid as a result of the following observations: (i) XXV absorbed 2 mol of hydrogen, indicating its bicyclic nature; (ii) dehydrogenation of XXV gave rise to 1,2,5-trimethylnaphthalene; (iii) methylation of the monoepoxide (XXVI) with methyl magnesium bromide followed by dehydrogenation resulted in the formation of 1,2,5,6-tetramethylnaphthalene, indicating that another double bond is at C-3. Compound XXIV was chemically correlated with II as follows. The alcohol formed upon removal of the C-7 oxygen function by Huang-Minlon reduction of the keto acetate (XXVII) was found to be identical with kolavenol (XXVIII), which was prepared by the reduction of XXV with lithium aluminum hydride; the comparison of their IR spectra, $[\alpha]_D$ and the mixed melting point test of their 3,5-dinitrobenzoate. The structure (XXV) thus established is in accordance with the constitution proposed for methyl kolavenate which has been isolated from *Hardwickia pinata* by Dev *et al.*[10] Although direct comparison of both substances has not been possible, it is evident that XXV is identical with methyl kolavenate, since the physical properties of both derivatives are in good agreement. Consequently, XXIV and XXVIII are named kolavenic acid and kolavenol, respectively. Kolavenol itself was also isolated from the dried root as its 3,5-dinitrobenzoate.

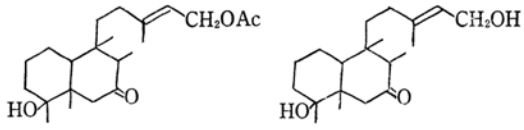
The stereochemistry of C-8 was assigned by an examination of solvent effects on the chemical shift of the secondary methyl group in the 7-keto derivatives. Downfield shifts of 0.06 and 0.05 ppm for XXVII and XXIX respectively were observed on changing solvent from carbon tetrachloride to benzene; these values are in reasonable agreement with those for equatorial methyl groups adjacent to a ketone. The equatorial orientation of the

7) T. G. Halsall, A. W. Oxford and W. Rigby, *Chem. Commun.*, **1965**, 218 and references therein.

8) E. J. Corey and J. J. Ursprung, *J. Am. Chem. Soc.*, **78**, 5041 (1956).

9) D. H. R. Barton, H. T. Cheung, A. D. Cross, L. M. Jackmann and M. Martin-Smith, *J. Chem. Soc.*, **1961**, 5061.

10) R. Misra, R. C. Pandey and Sukh Dev, *Tetrahedron Letters*, **1964**, 3751.



XXIX XXX

Fig. 7

C-8 methyl group was also supported by the fact that the starting ketodiol monoacetate (XXIX) was recovered by the treatment with alkali followed by acetylation.

The C-7 hydrogen appears as broad peaks or broad quartet-like peaks with half height width of 6—8 cps in the NMR spectra for 7-acetoxy or 7-hydroxy derivatives. These values suggest that C-7 hydrogen is in equatorial and thus the acetoxyl group should be axially oriented, since it has been demonstrated that the two adjacent carbon atoms (C-6 and 8) carry axial hydrogens.

The chemical shifts of the two tertiary methyl groups of the various derivatives prepared are summarized in Table 1. Remarkable upfield

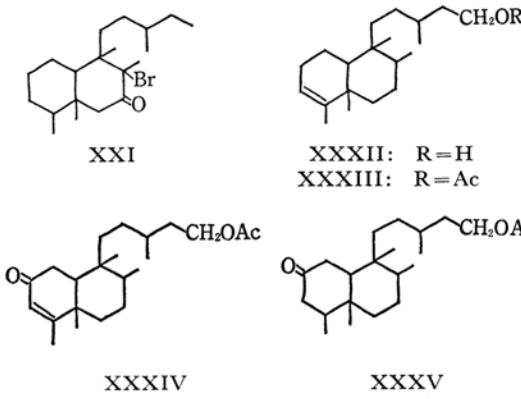
Table 1. Chemical shift (δ) of the tertiary methyl groups

Compound	Solv.	C-5 Me	C-9 Me
IV	CCl_4	1.25	0.98
IV	C_6H_5N	1.55	1.21
V	CCl_4	1.25	0.97
XXVII	CCl_4	0.95	0.71
XVI	CCl_4	1.27	1.01
XVIII	CCl_4	0.96	0.72

shifts (about 0.3 ppm) of both of these methyl groups were observed, when the C-7 hydroxyl group was converted to a ketone. Therefore, 1,3-diaxial relations are expected between the methyl groups and the C-7 hydroxyl group.[11] The signals of these methyl groups of the diol (IV) moved downward (0.30 and 0.23 ppm, respectively) when the solvent was changed from carbon tetrachloride to pyridine, in which the downfield shift due to 1,3-diaxial relationship is known to increase.[12] The acetoxyl group in II is in a sterically hindered environment. The evidences for this are based on the following observations; (i) the acetyl group in II and VI resists to alkaline hydrolysis—a period of 10 hr at refluxing temperature was required to complete the reaction in 20% methanolic potassium hydroxide, (ii) the C-7 hydroxyl group could not be acetylated readily and (iii) the triol monoacetate (XIII) was recovered on reduction of the ketodiol monoacetate (XXIX) with sodium borohydride, indicating an attack of the reagent from the opposite side of the original hydroxyl group. These observations lead to the conclusion that the two tertiary methyl groups and the acetoxyl group in II are in a 1,3,5-triaxial relation.

The allylic methyl group in the side chain of III appeared at δ 2.15 ppm in carbon tetrachloride and this signal shifted to 2.20 ppm in benzene. These values are in good agreement with those expected for the allylic methyl group which is *cis* to a carbomethoxyl group.[13]

The ring junction and the absolute configuration were determined by examination of the ORD curves of the 7-ketone (XXIII), the bromoketone (XXXI) and the 2-keto acetate (XXXV). Bromination of XXIII in carbon tetrachloride furnished a monobromoketone (XXXI) $C_{20}H_{35}OBr$,



XXI XXXII: R=H XXXIII: R=Ac

XXXIV XXXV

Fig. 8

which must be the 8-bromide, as the quartet of the C-8 proton disappeared and the singlet of the C-8 methyl group appeared at δ 1.72 ppm in its NMR spectrum. The axial orientation of the bromine was borne out by the facts that only a little shift ($+1\ cm^{-1}$) of the carbonyl band in IR spectrum was observed on bromination,[14] and that the NMR signal of one of the C-6 hydrogens showed a downfield shift which was probably due to the 1,3-diaxial interaction with the bromine atom.[15] This assignment was also confirmed by a bathochromic shift and an increasing amplitude of Cotton effect.[16] The ORD curve of the bromoketone (XXXI) showed a more intense negative Cotton effect ($a=-79.5$) in comparison with the 7-ketone (XXIII) which showed a small negative

11) N. S. Bacca and D. H. Williams, "Application of NMR Spectroscopy in Organic Chemistry," Holden-Day, San Francisco (1964), p. 19.

12) K. Tori and K. Aono, *Ann. Rept. Shionogi Res. Lab.*, **14**, 136 (1964).

13) J. Ronayne and D. H. Williams, *J. Chem. Soc., (C)*, **1967**, 2642.

14) R. N. Jones, D. A. Ramsay, F. Herling and K. Dobriner, *J. Am. Chem. Soc.*, **74**, 2828 (1952).

15) N. S. Bacca and D. H. Williams, "Application of NMR Spectroscopy in Organic Chemistry," Holden-Day, San Francisco (1964), p. 75, 183.

16) C. Djerassi, J. Osiecki, R. Riniker and B. Riniker, *J. Am. Chem. Soc.*, **80**, 1216 (1958).

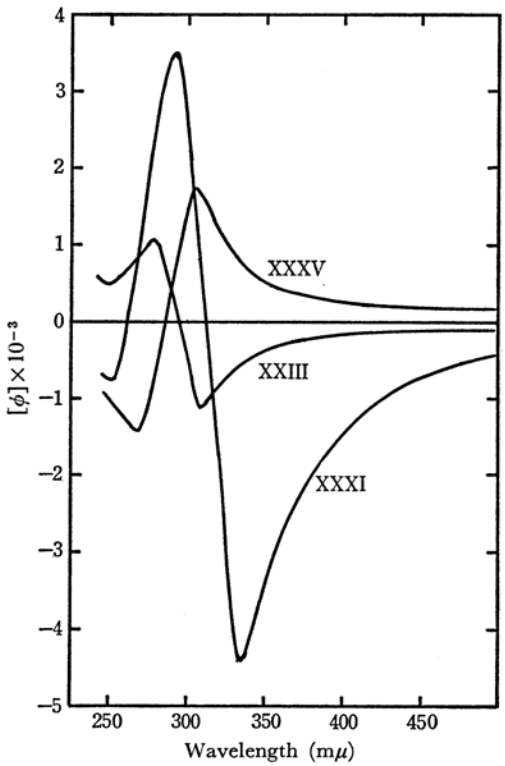


Fig. 9. ORD curves of XXIII, XXXI and XXXV.

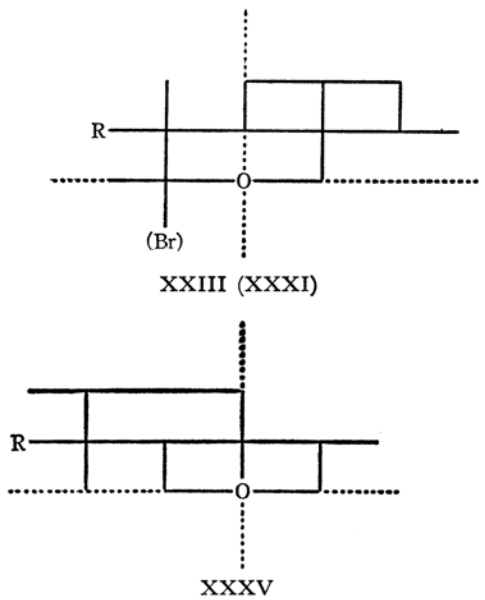


Fig. 10

Cotton effect ($a=-21.5$). Thus the bromine atom is β-oriented according to the axial haloketone rule and the absolute configuration of the B ring, except C-10, should be in the form given by II. The conjugated system in the side chain of methyl kolavenate (XXV) was reduced with metallic sodium in ethanol, and acetylation of the product afforded dihydrokolavenol acetate (XXXIII) $C_{22}H_{38}O_2$, bp 145—150°C (bath)/0.5 mmHg. Compound XXXIII was oxidized with chromium trioxide in acetic acid at 50°C to furnish an α,β-unsaturated cyclohexenone derivative (XXXIV): ν_{max}^{Oil} 1670, 1620 cm^{-1}; λ_{max}^{EtOH} 240 mμ (ε 9800); δ 1.85 3H d $J=1.2$ cps (C-4 methyl) and δ 5.56 1H d $J=1.2$ cps (C-3 proton). The newly introduced carbonyl group must be at C-2 as indicated by these spectral data. The 2-keto acetate (XXXV) $C_{22}H_{38}O_3$ was obtained by hydrogenation of XXXIV and reoxidation of the resultant saturated alcohol. The ORD curve of XXXV showed a positive Cotton effect ($a=+31.5$). Consequently, the *trans* junction of AB ring was established since the absolute configuration of the B ring, except C-10, was determined as mentioned above. Accordingly, the stereochemistry of solidagonic acid was fully established as shown by II.

Experimental

All melting points were measured on a Kofler block and are uncorrected. The NMR spectra were taken on a JEOL C-60 spectrometer in carbon tetrachloride unless otherwise stated; the signals are recorded in ppm from TMS (internal standard) as zero. All rotations were measured in 95% ethanol solution. Petroleum ether had bp 60—70°C. Merck silica-gel (0.05—0.2 mm) was used for chromatography.

Isolation of Solidagonic Acid (II). The sliced fresh root of *S. altissima* L. (11 kg) was extracted with ethanol at room temperature, the ethanol extract concentrated under reduced pressure and the residue extracted with ether. The oily residue (82 g) obtained after removing the solvent was chromatographed on silicagel (400 g) and eluted with benzene - ethyl acetate (95 : 5); 1.4 g of colorless crystals were obtained. The remaining oily portion was rechromatographed on a column of silicic acid (150 g), and eluted with benzene - ethyl acetate (98 : 2); 1.2 g of the crystals. The combined crystalline portion was recrystallized from petroleum ether to give colorless prisms: mp 143—144°C; $[\alpha]_D^{12}$ −97.6° (c 2.07); IR (KBr) 3400—2400, 1732, 1680, 1637, 1237 cm^{-1}; UV λ_{max}^{EtOH} 217.5 mμ (ε 9090); NMR 0.97, 1.17, 2.00 (each 3H s), 0.92 (3H d $J=7$ cps), 1.59, 2.18 (each 3H slightly splitting singlet), near 5.1 (2H broad peak), 5.63 (1H broad singlet), 11.75 (1H s).

Found: C, 72.88; H, 9.51%. Calcd for $C_{22}H_{34}O_4$: C, 72.89; H, 9.45%.

The methyl ester was obtained as granular crystals by esterification with diazomethane in ether and recrystallization from petroleum ether: mp 106.5°C; $[\alpha]_D^{12}$ −98.8° (c 1.80); IR (KBr) 1732, 1720, 1645, 1252, 1145 cm^{-1}; UV λ_{max}^{EtOH} 217.5 mμ (ε 15400); NMR 2.15 (3H d $J=1.2$ cps), 3.63 (3H s); NMR (in benzene) 2.20 (3H d $J=1.2$ cps).

Found: C, 73.22; H, 9.68%. Calcd for $C_{23}H_{36}O_4$: C, 73.36; H, 9.64%.

Isolation of Solidagonic Acid (III) and Kolavenic Acid (XXV) as Their Methyl Esters and of Kolavenol (XXVIII). The dried and crushed root (2.7kg) was

extracted with benzene by allowing to stand at room temperature for 4 weeks. The oily residue (90 g) obtained after removing the solvent under reduced pressure was partitioned between petroleum ether and 80% aqueous methanol.

An oil obtained by the evaporation of the solvent of the methanol-soluble fraction (36 g) was dissolved in ether and treated with an excess of diazomethane. The product was chromatographed on a silica-gel (400 g) column, and eluted with benzene, the eluate concentrated and the residue recrystallized from petroleum ether. Methyl solidagonate (III) was obtained as granular crystals (10 g), mp 106.5°C.

The petroleum ether solution, which had been extracted with 80% methanol, was again extracted with 95% methanol. An oily residue (23 g) left after removal of methanol was treated with an excess of diazomethane in ether. The resultant oil was chromatographed on a silica-gel (280 g) column and eluted with benzene. The first fraction was rechromatographed on a fresh silica-gel (100 g) column with petroleum ether - benzene (1 : 1) as a developing system. Methyl kolavenate (XXV) was obtained as a coloroess oil (8.1 g): bp 151—152°C/1 mmHg; $[\alpha]_D^{26}$ −60.8° (*c* 2.07); IR(oil) 1725, 1645, 1230, 1150 cm^{-1}; NMR 0.76, 1.02, 3.65 (each 3H s), 0.85 (3H d J=6 cps), 1.60 (3H slightly splitting singlet), 2.18 (3H d J=1.2 cps), 5.15 (1H broad), 5.59 (1H broad).

Found: C, 79.05; H, 10.87%. Calcd for $C_{21}H_{34}O_2$: C, 79.19; H, 10.76%.

The second fraction gave a small amount of III.

The third reaction was rechromatographed on a silica-gel column. Its elution with petroleum ether - ethyl acetate (95 : 5) gave an oil (0.5 g), which was treated with 3,5-dinitrobenzoyl chloride in pyridine to furnish kolavenol 3,5-dinitrobenzoate, mp 107°C. It was identified by mixed melting point with an authentic sample (prepared from methyl kolavenate) and by comparison of their IR spectra.

Reduction of III with Lithium Aluminum Hydride. A solution of III (3.5 g) in absolute ether (50 m*l*) was added dropwise to lithium aluminum hydride (1.7 g) in absolute ether (30 m*l*) with stirring, the mixture was stirred for further 4 hr under reflux, and then kept standing overnight. The reaction mixture was treated in the usual manner and the crude product was crystallized from benzene - petroleum ether, the diol (IV) was obtained as needles (2.6 g): mp 93.5—94.5°C; NMR 0.98, 1.25 (each 3H s), near 1.00 (3H d J=*ca.* 7 cps), 1.59 (3H d J=1.5 cps), 1.65 (3H slightly splitting singlet) near 3.94 (1H broad), 4.00 (2H d J=7 cps), 5.06 (1H broad) 5.31 (1H broad triplet J=7 cps); NMR (in pyridine) 1.21, 1.55 (each 3H s), 1.16 (3H d J=7 cps).

Found: C, 78.23; H, 11.16%. Calcd for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18%.

Hydrogenation of III. Compound III (6.4 g) in ethanol (120 m*l*) was hydrogenated over 5% palladium-charcoal (0.6 g) at room temperature and atmospheric pressure; 2 mol of hydrogen was absorbed during 3 hr. The product (VI) (6.4 g) could not be crystallized. NMR 0.92 (6H s), 1.94, 3.60 (each 3H s), 4.97 (1H braod W_h=*ca.* 8 cps).

Dehydrogenation of III. i) A mixture of III (1.0 g) and 10% palladium-charcoal (1.5 g) was heated at 280—300°C under nitrogen for 12 hr, extracted with ether, the solvent evaporated, and a saturated solution of 1,3,5-trinitrobenzene in ethanol added to the residue; the adduct of 1,2,5-trimethylnaphthalene was obtained as orange yellow needles (80 mg), mp 158°C.

Found: C, 59.82; H, 4.68; N, 10.70%. Calcd for $C_{19}H_{17}O_6N_3$: C, 59.53; H, 4.47; N, 10.96%.

ii) Methyl solidagonate (III) (3.0 g) was heated at 270—280°C for 6.5 hr with selenium (3.0 g) under nitrogen, the reaction mixture extracted with ether, the ether extract passed through a column of alumina (20 g) and the solvent of the eluate was evaporated to dryness. A saturated solution of picric acid in ethanol was added to the residue to give 1,2,5-trimethylnaphthalene picrate as reddish orange needles (290 mg), which was recrystallized from ethanol, mp 139—140°C. This picrate was decomposed on a silica-gel column to the corresponding hydrocarbon; NMR 2.40, 2.49, 2.60 (each 3H s).

Styphnate, mp 131°C

Monoepoxide (IX). Monoperphthalic acid (0.485 g, 1.0 equiv.) in ether (22 m*l*) was added to an ether solution of III (1.0 g in 20 m*l*) under stirring in an ice bath and the reaction mixture allowed to stand for 19 hr at room temperature. The reaction mixture was washed successively with a saturated aqueous solution of sodium bicarbonate and water and then dried. The crystalline residue obtained upon evaporation of the solvent was chromatographed on a silica-gel (20 g) column. Elution with benzene - ethyl acetate (95 : 5) gave the monoepoxide (IX) (0.9 g), which was recrystallized from petroleum ether to give colorless prisms: mp 135.5—136.5°C; IR(KBr) 1729, 1715, 1640 cm^{-1}; NMR 0.90 (3H d J=7.1 cps), 0.92, 1.15, 1.19, 1.99, 3.60 (each 3H s), 2.14 (3H d J=1.1 cps), 2.77 (1H triplet like), 5.05 (1H ill resolved quartet, W_h=*ca.* 6 cps), 5.53 (1H broad singlet).

Found: C, 70.40; H, 9.30%. Calcd for $C_{23}H_{36}O_5$: C, 70.37; H, 9.24%.

Grignard Reaction of IX. A solution of IX (3.0 g) in absolute ether (80 m*l*) was added dropwise to a solution of methyl magnesium bromide (which had been prepared from 4.7 g of magnesium in 150 m*l* of absolute ether). The mixture was stirred for 6 hr under reflux, and allowed to stand overnight. The oily product was chromatographed on a silica-gel (90 g) column. Elution with benzene - ethyl acetate (85 : 15) gave the epoxydiol (X) (0.3 g), which was recrystallized from petroleum ether to give colorless prisms: mp 104.5—106°C; NMR 2.80 (1H triplet like).

Found: C, 75.45; H, 11.08%. Calcd for $C_{22}H_{38}O_3$: C, 75.38; H, 10.93%.

Successive elution of the chromatogram with benzene-ethyl acetate (7 : 3) afforded the triol (XI) (0.7 g), which was recrystallized from petroleum ether, mp 85—89°C.

Found: C, 75.69; H, 11.44%. Calcd for $C_{23}H_{42}O_3$: C, 75.36; H, 11.55%.

Dehydrogenation of XI. Compound XI (0.49 g) was heated for 8.5hr at 290—300°C with 10% palladium-charcoal (0.5 g) in a nitrogen atmosphere, the reaction mixture extracted with ether and the solvent removed. The crude oily product upon treatment with picric acid in ethanol gave the picrate (0.08 g), which was decomposed on a silica-gel column to 1,2,5,6-tetramethylnaphthalene; the recrystallized product (from ethanol), mp 116—117°C. NMR 2.41, 2.51 (each 6H s), 7.11, 7.63 (each 2H d J=9 cps).

Found: C, 91.09; H, 8.91%. Calcd for $C_{14}H_{16}$:

C, 91.25; H, 8.75%.

Picrate, mp 155—156°C.

Reduction of IX with Lithium Aluminum Hydride. To lithium aluminum hydride (1.4 g) in absolute ether (20 m*l*) was added a solution of IX (1.0 g) in absolute ether (30 m*l*) during a 30 min period with stirring at room temperature. The mixture was stirred for further 6 hr under reflux and set aside over night at room temperature. The reaction mixture was terated in the usual manner and the crude product was crystallized from benzene, the triol (XII) (0.6 g) was obtained: mp 120—121.5°C; NMR (in $CDCl_3$) 1.70 (3H slightly splitting singlet), 4.14 (2H d J=6 cps), 5.40 (1H broad triplet J=6 cps).

Found: C, 74.12; H, 11.32%. Calcd for $C_{20}H_{36}O_3$: C, 74.02; H, 11.18%.

Triol Monoacetate (XIII). Compound XII (1.0 g) dissolved in pyridine (8 m*l*) was treated with acetic anhydride (4 m*l*), and the reaction mixture set aside 17 hr at room temperature. Recrystallization from benzene gave XIII as prisms (1.0 g): mp 142.5—143.5°C; IR (KBr) 3500, 1712, 1240 cm^{-1}; NMR (in $CDCl_3$) 2.08 (3H s), 4.09 (1H ill resolved quartet), 4.59 (2H d J=7.5 cps), 5.37 (1H broad triplet J=7.5 cps).

Found: C, 72.11; H, 10.52%. Calcd for $C_{23}H_{38}O_4$: C, 72.09; H, 10.45%.

Triol Diacetate (XIV). Compound XIII (1.0 g) in pyridine (10 m*l*) and acetic anhydride (4 m*l*) was heated 100°C for 4hr. The oily product was chromatographed on a silica-gel (30 g) column. Elution with benzene - ethyl acetate (85 : 15) gave the oily diacetate (XIV) (0.85 g): IR(oil) 3500, 1740 (broad), 1230 cm^{-1}; NMR 1.97 (6H s), 5.09 (1H broad.)

Successive elution with the same solvent afforded the starting monoacetate (XIII) (0.2 g).

Ozonolysis of XIV. Ozonized oxygen was passed through a solution of XIV (0.83 g) in chloroform (14 m*l*) under ice-salt cooling for 25 min. The solvent was evaporated *in vacuo* and the oily residue was heated with 20 m*l* of water on a boiling water bath for 30 min. The neutral oil (0.6 g) obtained was chromatographed on a silica-gel (15 g) column with benzene - ethyl acetate (7 : 3) as a developing solvent. The crude methyl ketone (XV) (0.35 g) thus obtained was recrystallized from petroleum ether: mp 104—105°C; IR(KBr) 3540, 1732, 1705, 1232 cm^{-1}; NMR 1.99, 2.10 (each 3H s), 5.05 (1H quartet like W_h=*ca.* 7 cps).

Found: C, 70.75; H, 10.08%. Calcd for $C_{20}H_{34}O_4$: C, 70.97; H, 10.13%.

Keto Ester (XVIII). Compound II (1.0 g) was heated under reflux in 20% methanolic potassium hydroxide (20 m*l*) for 9.5 hr. The hydroxy acid (XVI) obtained as an oil (0.9 g) could not be crystallized after chromatography on a silica-gel column: IR(oil) 3360, 3200—2400, 1685, 1635 cm^{-1}; NMR 1.01, 1.27 (each 3H s), 4.00 (1H broad W_h=7.5 cps).

Jones reagent [a mixture of chromium trioxide (2.7 g) and concentrated sulfuric acid (2.3 m*l*) in water (10 m*l*)] (1.0 m*l*) was added dropwise to a solution of XVI (0.9 g) in acetone (30 m*l*) in an ice bath. The mixture was stirred for 2hr, diluted with water and extracted with ether. The ether solution was concentrated and treated with a solution of diazomethane in ether. Chromatography on a silica-gel (20 g) column with benzene gave the keto ester (XVIII) as an oil (0.65 g): IR(oil) 1710 (broad), 1640, 1225, 1150 cm^{-1}; NMR 0.72, 0.96 (each 3H s).

2, 4-Dinitrophenylhydrazone, mp 174°C.

Found: C, 63.22; H, 7.19; N, 10.86%. Calcd for $C_{27}H_{36}O_6N_4$: C, 63.26; H, 7.08; N, 10.93%.

Tetrahydro-hydroxy Esters (VIIa, b) and hydroxy Acids (VIIIa, b). Compound VI (7.0 g) was heated under reflux in 5% ethanolic potassium hydroxide for 8 hr. The acidic fraction was treated with an excess of diazomethane in ether for 3hr at room temperature. The oily product (6.5 g) obtained by evaporation of the solvent was chromatographed on a silica-gel (150 g) column and eluted with benzene - ethyl acetate (95 : 5). The oily hydroxy ester (VIIa) (3.6 g, a single spot on TLC) was isolated: IR (oil) 3510, 1740, 1200, 1010 cm^{-1}; IR (in CCl_4) 3680, 3500, 1745, 1200, 1010 cm^{-1}.

Successive elution with the same solvent gave a mixture of the two esters (0.8 g) and the crystalline hydroxy ester (VIIb) (1.8 g). The latter was recrystallized from petroleum ether: mp 84—87°C; IR(KBr) 3500, 1720, 1195, 1000 cm^{-1}.

Found: C, 74.69; H, 11.13%. Calcd for $C_{21}H_{38}O_3$: C, 74.51; H, 11.32%.

The IR spectra for VIIa and VIIb in carbon tetrachloride were almost iden tical.

Compound VIIa (2.2 g) was hydrolyzed for 3hr with 8% ethanolic potassium hydroxide under reflux. The hydroxy acid (VIIIa) was isolated in the usual manner and recrystallized from ptroleum ether as colorless plates (2.0 g): mp 99—100°C; IR (in $CHCl_3$) 3600, 3500, 3300—2500, 1710 cm^{-1}.

Found: C, 74.07; H, 11.24%. Calcd for $C_{20}H_{36}O_3$: C, 74.02; 11.18%.

Compound VIIb was hydrolyzed to the hydroxy acid (VIIIb), which was recrystallized from petroleum ether - benzene (8 : 2) as hexagonal plates, mp 142—144°C.

Found: C, 74.28; H, 10.97%.

The IR spectra for VIIIa and VIIIb in chloroform were almost identical.

Oxidation of VIIIb with Jones Reagent. Jones reagent (4.0 m*l*) was added to a solution of VIIIb (3.5 g) in acetone (80 m*l*) during a course of 10 min in an ice bath with stirring and the mixture was stirred for further 30 min at this temperature. The reaction mixture was treated in a usual manner and the crude product was crystallized from petroleum ether. The tetrahydro-keto acid (XIX) was obtained as needles (2.9 g), mp 82—83°C.

Found: C, 74.63; H, 10.71%. Calcd for $C_{20}H_{34}O_3$: C, 74.49; H, 10.63%.

The Reaction of XIX With Methyl Magnesium Bromide. A solution of XIX(3.5 g) in absolute ether was added dropwise to methyl magnesium bromide (which had been prepared from 1.1 g of magnesium) in absolute ether under constant stirring, the mixture heated under reflux for 6 hr, and then the reaction mixture treated as usual. The product was chromatographed on a silica-gel (60 g) column. Its elution with benzene - ethyl acetate (4 : 1) afforded the hydroxy acid (XX) (1.3 g), which was recrystallized from petroleum ether as needles: mp 128.5—130.5°C; IR(KBr) 3460, 3200—2400, 1711 cm^{-1}.

Found: C, 74.45; H, 11.36%. Calcd for $C_{21}H_{38}O_3$: C, 74.51; H, 11.32%.

Dehydrogenation of XX with Selenium. A mixture of XX (1.3 g) and selenium (1.3 g) was heated at 300°C for 10 hr under nitrogen and the reaction mixture

extracted with petroleum ether. The petroleum ether solution was passed through a column of silica-gel (20 g) to give a fraction, which on addition of a saturated solution of picric acid in ethanol, afforded the adduct (192 mg) of 1,2,3,5-tetramethylnaphthalene as orange-red crystals, mp 163—164°C. This adduct was decomposed on a silica-gel column to the corresponding hydrocarbon; NMR 2.32, 2.42, 2.54, 2.62 (each 3H s).

1,3,5-Trinitrobenzene adduct, mp 182—183°C.

Found: C, 60.67; H, 5.12; N, 10.49%. Calcd for $C_{20}H_{19}O_6N_3$: C, 60.45; H, 4.82; N, 10.58%.

7-Ketone (XXIII). Compound IV (2.6 g) in acetic acid (100 m*l*) and ethanol (50 m*l*) was hydrogenated over Adams catalyst (200 mg) at room temperature under atmospheric perssure; about 2.9 mol of hydrogen was absorbed. The oily product (2.6 g) obtained was chromatographed on a silica-gel (20 g) column and eluted with benzene. The 7-monoalcohol (XXII) was obtained as a colorless oil (1.6 g): IR(oil) 3350 cm^{-1}; NMR 3.95 (1H quartet like).

Jones reagent (2.0 m*l*) was added to a solution of XXII (1.6 g) in acetone (30 m*l*) in 3 min in an ice bath, stirred for further 10 min at this temperature, and the reaction mixture worked up in the usual way. Distillation of an oily product under reduced pressure afforded 7-ketone (XXIII) (1.6 g): bp 125—133°C (bath)/1 mmHg; IR(oil) 1708 cm^{-1}; NMR 1.94, 2.28 (each 1H d J=12 cps), 2.45 (1H q J=6.7 cps); ORD $[\phi]_{308}^{trough}$ −1145°, $[\phi]_{278}^{peak}$ +1007° (*c* 0.147, in CH_3OH).

Found: C, 82.07; H, 12.35%. Calcd for $C_{20}H_{36}O$: C, 82.12; H, 12.40%.

Dehydrogenation of XXV. Compound XXV (1.6 g) was heated for 10 hr with 10% palladium-charcoal (1.0 g) at 300—320°C under nitrogen and the mixture was extracted with ether. An oil (1.0 g) obtained after removal of the solvent was treated with picric acid in ethanol. Reddish brown crystalls of 1,2,5-trimethylnaphthalene picrate were recrystallized from ethanol; yield 109 mg, mp 136—138°C which was undepressed on admixture with the authentic sample.

Hydrogenation of XXV. Compound XXV (1.6 g) was dissolved in ethanol (50 m*l*) and hydrogenated over Adams catalyst (0.2 g); 2.04 mol of hydrogen was absorbed during a 2.5 hr period. The product was isolated as usual and distilled under reduced pressure: bp 135—140°C (bath)/3 mmHg; IR (oil) 1745, 1160 cm^{-1}.

Methyl Kolavenate Monoepoxide (XXVI). A solution of monoperphthalic acid (3.3 g, 1.1 equiv.) in ether (140 m*l*) was added dropwise to a solution of XXV (5.0 g) in ether (50 m*l*) with stirring in an ice bath. The mixture was set aside for 20 hr at room temperature. Working up in the usual way gave a colorless oil (5.4 g), which was chromatographed on a silica-gel (100 g) column. Elution with benzene - ethyl acetate (95 : 5) afforded the monoepoxide (XXVI) as an oil (4.55 g): IR(oil) 1720, 1645 cm^{-1}; NMR 0.69, 1.06, 1.15, 3.64 (each 3H s), 2.16 (3H d J=1.2 cps), 2.78 (1H triplet like), 5.60 (1H broad singlet).

Grignard Reaction of XXVI Followed by Dehydrogenation. A solution of XXVI (4.3 g) in absolute ether (40 m*l*) was added dropwise to an ice cold solution of methylmagnesium bromide (which had been prepared from 4.7 g of magnesium) in absolute ether (100 m*l*). The mixture was stirred under reflux for 6.5 hr and set aside overnight at room temperature. Working up in the usual way afforded an oily product (4.5 g). A mixture of this oil (2.4 g) and selenium (2.0 g) was heated at 300—320°C for 8 hr under nitrogen and after cooling extracted with ether. The ether solution was passed through a column of alumina and the solvent of the eluate evaporated. The residue was recrystallized from ethanol to give 1,2,5,6-tetramethylnaphthalene; mp 115—116°C, picrate mp 157—157.5°C.

Kolavenol (XXVIII). A solution of XXV (3.2 g) in absolute ether (50 m*l*) was added dropwise to a solution of lithium aluminum hydride (1.0 g) in absolute ether (100 m*l*) in 15 min at room temperature and the mixture refluxed for 3 hr. Working up the reaction mixture in the usual way afforded an oil (3.0 g), which was chromatographed on a silica-gel (60 g) column. Elution with benzene - ethyl acetate (95 : 5) gave kolavenol (XXVIII) as an oil (1.5 g), $[\alpha]_D^{26}$ −57.1° (*c* 2.52).

The 3,5-dinitrobenzoate derivative was prepared by treatment with 3,5-dinitrobenzoyl chloride and pyridine, and recrystallized from ethanol, mp 105.5—106.5°C.

Found: C, 66.90; H, 7.49; N, 5.94%. Calcd for $C_{27}H_{36}O_6N_2$: C, 66.92; H, 7.49; N, 5.78%.

Acetylation of IV Followed by Oxidation. Compound IV (1.0 g) was dissolved in a mixture of pyridine (8 m*l*) and acetic anhydride (4 m*l*) and set aside for 40 hr in a refrigerator. The oily product obtained in the usual way was chromatographed on a silica-gel (19 g) column to remove a small amount of the diacetate. Elution with benzene - ethyl acetate afforded the monoacetate (V) as an oil (1.1 g): IR(oil) 3500, 1740, 1235 cm^{-1}; NMR 0.97, 1.25, 1.97 (each 3H s), 3.96 (1H quartet like), 4.48 (2H d J=7.5 cps).

Compound V (1.1 g) in acetone (25 m*l*) was oxidized with Jones reagent (1.2 m*l*) in an ice bath. Working up the reaction product in the usual way and chromatography on a silica-gel column afforded the keto-acetate (XXVII) as an oil (0.85 g): NMR 0.71, 0.95 (each 3H s), 0.89 (3H d J=*ca.* 7 cps); NMR (in benzene) 0.95 (3H d J=7.2 cps).

Huang-Minlon Reduction of XXVII. A solution of XXVII (0.9 g) in triethyleneglycol (15 m*l*) containing potassium hydroxide (2.5 g) and 80% hydrazine hydrate (5 m*l*) was heated for 1 hr at 130°C, for 2 hr at 150°C and then for 1.5 hr at 210°C. The reaction mixture was extracted with ether and the ether solution was washed thoroughly with water, dried, and evaporated. The residual oil was chromatographed on a silica-gel (16 g) column and eluted with benzene - ethyl acetate (97 : 3); an oily alcohol yield 0.2 g, $[\alpha]_D^{27}$ −55.9°C (*c* 3.04). The IR spectrum of this alcohol was identical with that of kolvavenol (XXVIII) prepared from XXV.

The 3,5-dinitrobenzoate derivative, mp 105—106°C, showed no depression of melting point on admixture with authentic kolavenol 3,5-dinitrobenzoate.

Oxidation of XIII with Jones Reagent. Jones reagent (1.0 m*l*) was added to a solution of XIII (1.0 g) in acetone (20 m*l*) under stirring in an ice bath, and stirred for further 20 min at this temperature. Working up the reaction mixture in the usual way afforded the ketodiol monoacetate (XXIX) as a viscous oil (1.0 g), which could not be crystallized even after

careful chromatography on a silica-gel column. IR (oil) 3500, 1740, 1710, 1240 cm^{-1}; NMR 0.67, 0.91, 1.08, 1.98 (each 3H s), 0.87 (3H d J=6 cps); NMR (in benzene) 0.92 (3H d J=6 cps).

The Alkaline Treatment and Reduction with Sodium Borohydride of XXIX. Compound XXIX (0.7 g) was dissolved in 5% pottasium hydroxide solution in methanol (10 m*l*) and heated under reflux for 2 hr. The solution was concentrated *in vacuo* to half of its volume, diluted with water, and extracted with ether. The ketodiol (XXX) was obtained as a viscous oil (0.5 g), which could not be crystallized.

Compound XXX (0.5 g) was dissolved in pyridine (1 m*l*) and acetic anhydride (2 m*l*) and set aside overnight at room temperature. Working up the reaction mixture in the usual way afforded an oil (0.5 g), and its IR spectrum was identical with that of the starting ketodiol monoacetate (XXIX).

The ketodiol monoacetate (0.5 g) thus obtained was dissolved in methanol (15 m*l*) and sodium borohydride (0.1 g) was added in portions in an ice bath with stirring during 20 min. The mixture was stirred for 2 hr at room temperature, then acidified with acetic acid, and diluted with water to give colorless crystals. Recrystallization from benzene gave the pure crystals (0.4 g), which were found to be identical with authentic triol monoacetate (XIII) as shown by their melting point, mixed melting point and IR spectra.

Bromoketone (XXXI). A solution of bromine (0.10 m*l*) in carbon tetrachloride (4 m*l*) was added dropwise in 20 min to a solution of XXIII (0.5 g) in carbon tetrachloride (20 m*l*) at room temperature under stirring. The solution was stirred for further 30 min, and washed successively with water, aqueous sodium thiosulfate solution and water. Evaporation of the solvent gave a pale yellow oil (0.65 g), which was chromatographed on a silica-gel (14 g) column. Elution with petroleum ether - benzene (1 : 1) afforded the bromoketone (XXXI) as a colorless oil (0.5 g): IR(oil) 1709 cm^{-1}; NMR 1.72 (3H s), 2.21, 3.34 (each 1H d J=12.5 cps); ORD $[\phi]_{335}^{trough}$ −4450°C, $[\phi]_{292}^{peak}$ 3500° (c 0.119, in CH_3OH).

Found: C, 64.60; H, 9.59%. Calcd for $C_{20}H_{35}OBr$: C, 64.67; H, 9.50%.

Dihydrokolavenol Acetate (XXXIII). Metallic sodium (6 g) was added in portions to a boiling solution of XXV (3.1 g) in absolute ethanol (65 m*l*) during 2 hr. The mixture was kept at 100°C for 1.5 hr (during this period all sodium dissolved), cooled, diluted with water and then extracted with ether. The reddish brown oil (2.1 g) obtained on concentration was acetylated with acetic anhydride and pyridine and the product was chromatographed on a silica-gel (42 g) column with benzene as an eluting solvent. The dihydrokolavenol acetate (XXXIII) was obtained as an oil (1.9 g), which was distilled under reduced pressure: bp 145—150°C (bath)/0.5 mmHg; NMR 1.54 (3H d J=1.6 cps), 1.94 (3H s), 4.01 (2H t J=6.3 cps), 5.08 (1H broad).

Found: C, 79.13; H, 11.26%. Calcd for $C_{22}H_{38}O_2$: C, 78.98; H, 11.45%.

Oxidation of XXXIII with Chromium Trioxide. A solution of XXXIII (1.7 g) and chromium trioxide (1.4 g) in acetic acid (30 m*l*) and water (1.5 m*l*) was heated for 2 hr at 50°C. After an excess reagent was decomposed with ethanol, the solvent was evaporated *in vacuo*. An oily residue was dissolved in ether, the ether solution washed successively with water, a saturated aqueous solution of sodium bicarbonate and water, and dried. The oil obtained on evaporation of the solvent was chromatographed on a silica-gel column and eluted with benzene - ethyl acetate (9 : 1). The 2-keto-3-ene (XXXIV) was obtained as a pale yellow oil (0.5 g): IR(oil) 1738, 1670, 1620, 1235 cm^{-1}; UV λ_{max}^{EtOH} 240 mμ (ε 9800); NMR 1.85 (3H d J=1.2 cps), 1.96 (3H s), 4.02 (2H t J=6.3 cps) 5.56 (1H d J=1.2 cps).

2-Ketone Acetate (XXXV). Compound XXXIV (0.45 g) in ethanol (20 m*l*) was hydrogenated over Adams catalyst (40 mg) at room temperature and atmospheric pressure; 2.2 mol of hydrogen was absorbed. The product was isolated as a colorless oil (0.4 g), IR(oil) 3400 cm^{-1}.

The hydrogenation product (0.45 g) in acetone (10 m*l*) was oxidized with Jones reagent (0.5 m*l*) in an ice bath. An oily product was chromatographed on a silica-gel (14 g) column and eluted with benzene - ethyl acetate (9 : 1). The 2-ketone acetate (XXXV) was obtained as a colorless oil (0.25 g), which was distilled under reduced pressure: bp 168—173°C (bath)/0.006 mmHg; IR(oil) 1736, 1710, 1235 cm^{-1}; ORD $[\phi]_{305}^{peak}$ +1740°, $[\phi]_{268}^{trough}$ −1410° (c 0.116, in CH_3OH).

Found: C, 75.18; H, 10.91%. Calcd for $C_{22}H_{38}O_3$: C, 75.38; H, 10.93%.

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