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TERPENOIDS—LXVIII

STRUCTURE AND ABSOLUTE CONFIGURATION OF COSTIC ACID—A NEW SESQUITERPENIC ACID FROM COSTUS ROOT OIL*

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Abstract—The acidic fraction of costus root oil is composed of several acids, one of which, costic acid, has been obtained in the pure crystalline form via its amine salts. By systematic chemical degradation, spectral studies and subsequent conversion to dihydroeudesmol (XIII), the structure and absolute configuration of costic acid have been determined as I. It is the acid corresponding to costol (II), the selinenic allylic alcohol previously isolated by Sorm. Costol fraction of costus root oil has also been shown to be composed of several components, one of which can be converted to costic acid.

Costus root oil is known to contain acidic constituents which have been preliminarily examined by Semmler[1] and Sorm *et al.*[2] Possibly because of paucity of raw materials they were unable to isolate the constituents in the pure form and to determine their structures. As a result of large scale processing of costus root oil obtained by the low temperature solvent extraction procedure developed in our laboratory,[3] we were in possession of substantial amount of costus acids. These were initially obtained by controlled extraction of partially delactonized costus root oil with caustic alkali. The regenerated acids were then subdivided into sodium bicarbonate-soluble and sodium carbonate-soluble fractions. The bicarbonate extracts contained mostly hydroxy acids which will be dealt with in a separate communication. The carbonate soluble portion was found to contain four major components in nearly equal proportion, along with traces of two other components as revealed by GLC and TLC analyses. This acidic fraction on cooling at −18° in acetone solution deposited a mixture of palmitic and behenic acids. The residual mixture of acids contained in the mother liquor consisted mainly of three acids, from which by step-wise crystallization of cyclohexylamine and dicyclohexylamine salts, a pure crystalline acid could be obtained. Because of its structural relationship with costol, we propose to name it as "costic acid" and present evidences to show that its structure and absolute configuration are represented by the structure I.

Costic acid, $C_{15}H_{22}O_2$, on catalytic hydrogenation showed the presence of two double bonds, and is therefore, bicyclic. The IR spectrum (Fig. 1) showed bands at 1681 (carboxyl group conjugated with a double bond), 1634 (end methylene group) and 1613 cm^{-1} (conjugated methylene group). The UV spectrum also showed absorption for an α,β-unsaturated carboxyl group (λ_{max} 210 mμ; ε 5600). Methyl

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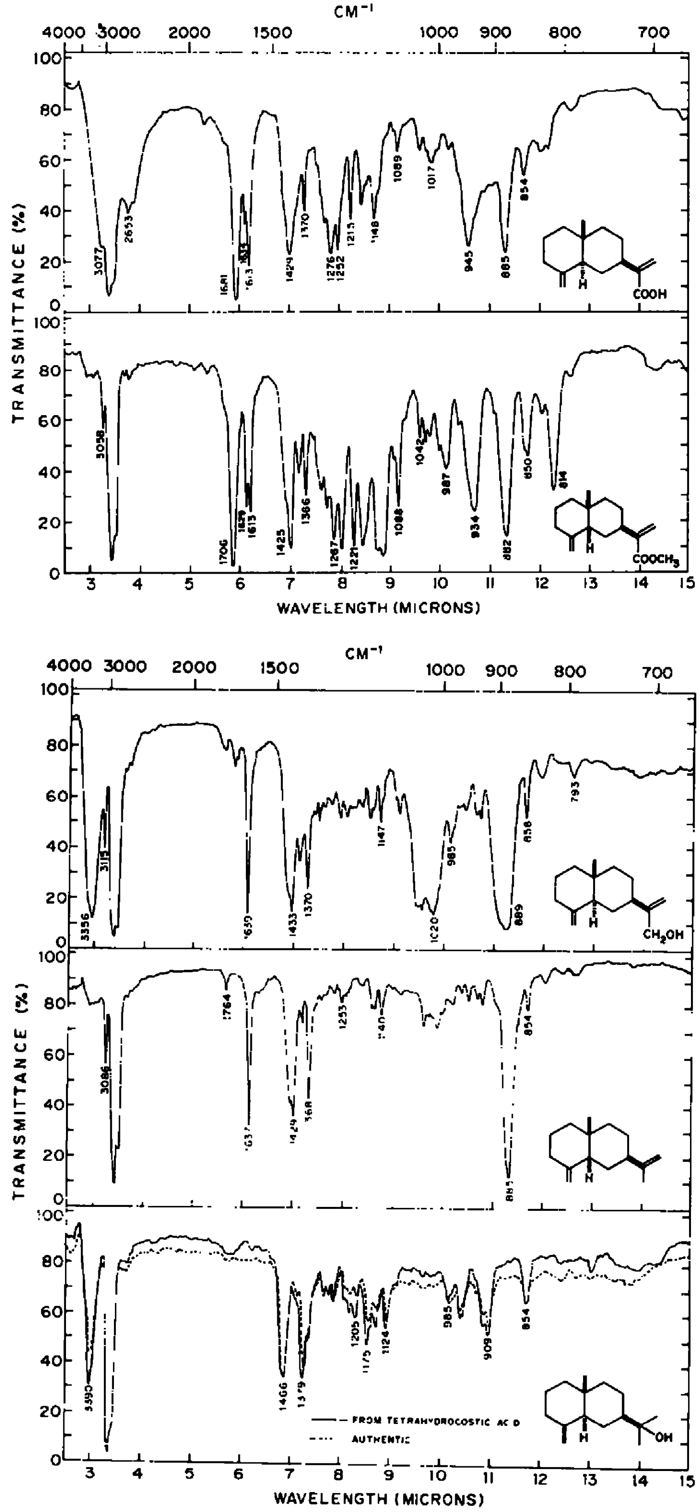
[*] Communication No. 761 from the National Chemical Laboratory, Poona-8, India.

[1] F. W. Semmler and Feldstein, *Ber. Dtsch. Chem. Ges.* **47**, 2433, 2687 (1914).

[2] M. Romanuk, V. Herout and F. Sorm, *Coll. Czech. Chem. Commun.* **23**, 2188 (1958).

[3] A. Paul, A. S. Bawdekar, R. S. Joshi, G. H. Kulkarni, A. S. Rao, G. R. Kelkar and S. C. Bhattacharyya, *Perf. and Ess. Oil Rec.* **51**, 115 (1960).


CM⁻¹
4000
3000
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TRANSMITTANCE (%)
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80
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1681
1613
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1276
1252
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1148
1089
1017
945
885
854
H
COOH
3058
1706
1629
1613
1425
1366
1267
1221
1088
1042
987
934
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850
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WAVELENGTH (MICRONS)
3356
3115
1639
1433
1370
1147
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Fig. 1

ester of costic acid also supports the α,β-unsaturated nature of the carboxyl group from its IR (Fig. 1) and UV absorption. The NMR spectrum (Fig. 2) of the methyl ester shows signals at 0·75 δ (3H) due to quarternary methyl at C_{10}; 3·70 δ (3H) due to ester methyl group; 4·37, 4·63 δ (2H) due to olefinic protons of the exomethylene group at C_4 and at 5·48 and 6·03 δ (2H) due to two protons conjugated with the ester carbonyl group.

This is in complete agreement with the structure Ia.

Selenium dehydrogenation of the acid gave 30% yield of a naphthalenic hydrocarbon identified as 1-methyl, 7-ethyl naphthalene[4] (III). The formation of this compound accounts for 13 of the 15 carbon atoms present in the acid. Of the remaining two, one can be accounted as an angular methyl group which is eliminated during dehydrogenation and the other, lost due to decarboxylation. From this it can be assumed that the carboxyl group occurs in the isopropyl side chain.

The methyl ester of costic acid (Ia) on reduction with LAH gave an alcohol, $C_{15}H_{24}O$, which from GLC analysis showed two peaks. NMR spectral studies indicated the presence of an extra methyl group, suggesting that some dihydro product was formed during reduction. The desired alcohol (IIa), which is evidently identical with costol (II), was obtained by reduction of the methyl ester with LAH–$AlCl_3$ complex.[5] The product, $C_{15}H_{24}O$, thus obtained showed a single peak in GLC and the NMR spectrum (Fig. 2) of the alcohol has signals at 0·74 δ (3H) due to angular methyl group at C_{10}, at 4·66 and 4·38 δ (2H) due to olefinic protons of the exomethylene group at C_4, at 4·96 and 4·85 δ (2H) due to olefinic protons of the dissymmetrically disubstituted protons at C_{11} and a multiplet at 4·03 δ (2H) was also observed due to two protons of the allylic—CH_2OH group. This is in complete agreement with the expected structure. On oxidation with Jones'[6] reagent the alcohol (IIa) gave an aldehyde (IV) in 75% yield (λ_{max} 216 mμ, ε 17,240), the semicarbazone of which melted at 223°. The semicarbazone showed characteristic UV absorption (λ_{max} 262 mμ, ε 26,530) for a diene system, thus further confirming that the parent alcohol IIa is an allylic alcohol and consequently costic acid is an α,β-unsaturated acid. A mixed m.p. (215°) of the semicarbazone of this aldehyde with that of costol (218°) was slightly depressed. This is understandable as from GLC study using substantial amount of natural "costol" it has been found by us that though, the structural and stereochemical assignments of Sorm *et al.*[7] regarding costol are correct, "costol" obtained from costus root oil is not homogenous, but consists mainly of two components in almost equal proportions along with traces of a third product. It is, thus possible that the semicarbazone obtained from natural costol is not pure and may be contaminated with closely related products. In agreement with this, the costol fraction of costus root oil after oxidation with Jones' reagent, followed by treatment with silver oxide gave a crystalline acid identical in all respects with costic acid.

The allylic alcohol IIa, on reduction with lithium in liquid ammonia[8] gives a hydrocarbon in 80% yield. This has been identified as (+) β-selinene (V), from its physical properties, specific rotation,* IR and NMR spectra. In the NMR spectrum

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[4] A. Somasekar Rao, G. R. Kelkar and S. C. Bhattacharyya, *Tetrahedron* **9**, 275 (1960).

[5] M. J. Jorgenson, *Tetrahedron Letters* No. **13**, 559 (1962).

[6] K. Bowden, I. M. Heilbron, E. R. Jones and B. C. L. Weeden, *J. Chem. Soc.* 39 (1946); C. Djerassi, R. R. Engle and A. Bowers, *J. Org. Chem.* **21**, 1547 (1956).

[7] V. Benesova, V. Herout and F. Sorm, *Coll. Czech. Chem. Commun.* **24**, 2365 (1959).

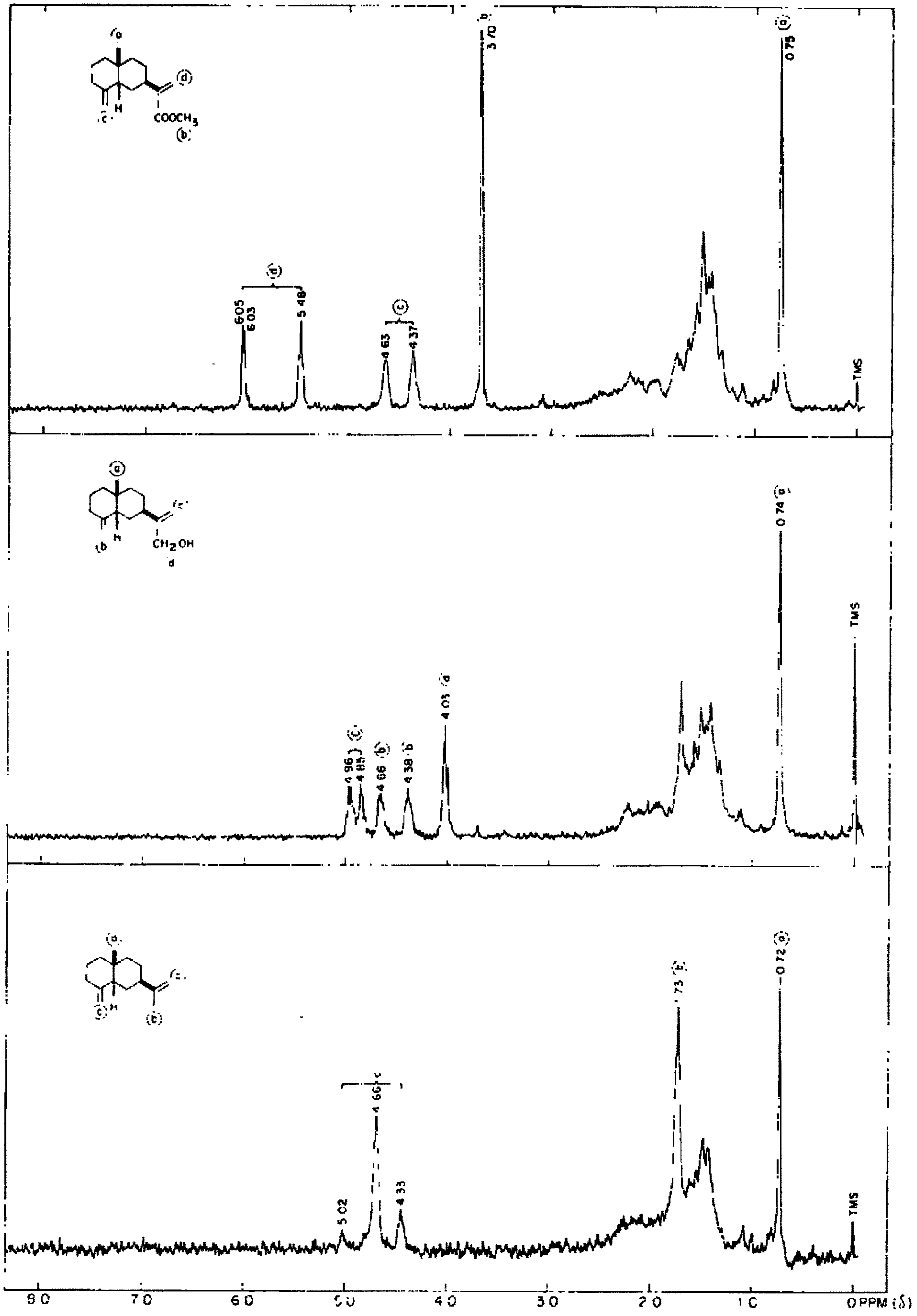

(a)
(d)
H
(c)
COOCH₃
(b)
6.05
6.03
(d)
5.48
4.63
(c)
4.37
3.70 (b)
0.75 (a)
TMS
(a)
(c)
H
(b)
CH₂OH
(d)
4.96
4.85
(c)
4.66 (b)
4.38 (b)
4.03 (d)
0.74 (a)
TMS
(a)
(c)
(c)
H
(b)
5.02
4.66 c
4.33
1.73 (b)
0.72 (a)
TMS
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0 PPM (δ)

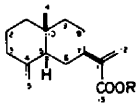
FIG. 2

(Fig. 2), it shows signals at 0·72 δ (3H) due to angular methyl group at C_{10}, at 1·73 δ (3H) due to a methyl group on a double bond at C_{11}, signals at 4·33, 4·66 and 5·02 δ (4H) were due to olefinic protons at C_4 and C_{11}. In conformity with its structure, the alcohol IIa on hydrogenation in presence of palladized carbon in ethanol solution gave as a result of hydrogenolysis, a saturated hydrocarbon in 50% yield. This was identified as selinane (VI) from mixed GLC and IR spectrum.

On ozonization, methyl costate gave a keto carboxylic acid, identified as VII, by m.p. (236°) of the semicarbazone of its methyl ester. This acid has been previously obtained by Sorm by ozonization of costol. From all these evidences, it is clear that costic acid is represented by the structure I.

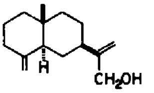
Costic acid on hydrogenation in ethanol in presence of Adams PtO_2 catalyst gave tetrahydro costic acid (VIII), which did not solidify. Degradation of tetrahydrocostic acid to dihydroeudesmol has been achieved.

Tetrahydrocostic acid, on treatment with methyl lithium in dry ether, was converted into the methyl ketone IX. The latter on Baeyer–Villiger oxidation with perbenzoic acid at room temperature gave the acetate (X). On saponification, it yielded the alcohol (XI) which on oxidation with Jones chromic acid reagent afforded the C_{14}-ketone (XII). This ketone was characterized as its semicarbazone, m.p. 206–207° agreeing with that reported in literature.[9]



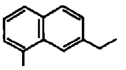
I R = H

I a R = CH_3



II Natural Costol

II a Costol from I



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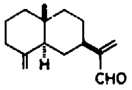

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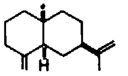

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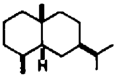

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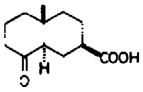

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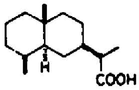
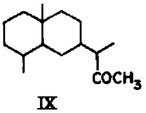
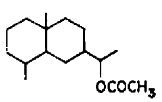


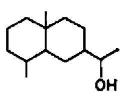
VIII



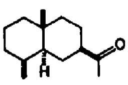
IX



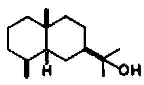
X



XI



XII



XIII

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[*] It may specially be mentioned that the β-selinene obtained from costic acid via costol shows high specific rotation (+59·51°), which must be due to its high isomeric purity. The highest value recorded in the literature is +40·0°. (R. Stevens, *J. Chem. Soc.* 956 (1964.)

[8] H. Bruderer, D. Arigoni and O. Jeger, *Helv. Chim. Acta* **39**, 858 (1956).

[9] K. Tanabe, *Pharm. Bull. Japan* **6**, 214 (1958).

On treatment with MeMgI in dry ether, the C_{14}-ketone (XII) was converted in good yield, into dihydroeudesmol (XIII), m.p. 83–85°; $(\alpha)_D^{27}$ +15·6°; mixed melting point with authentic sample was undepressed, and the IR spectra (Fig. 1) of both the samples were superimposable. This proves conclusively the stereochemistry of tetrahydrocostic acid (VIII) at all the centres and hence that of the parent compound costic acid (I).

EXPERIMENTAL

All m.ps and b.ps are uncorrected. Specific rotations were determined in $CHCl_3$ solution. UV absorption spectra were measured in EtOH (95%) solution with a Beckman Model DK-2 ratio recording spectrophotometer. IR spectra were taken with the Perkin–Elmer (Model 137b) Infracord spectrophotometer. GLC analyses were carried out using at least two stationary phases employing a Griffin MK-II model and Perkin–Elmer analyser. NMR spectra were measured with a Varian A-60 spectrometer operating at 60 mc with tetramethylsilane as internal reference.

Isolation of costic acid. Partially delactonized costus root oil[*] (500 g; acid value 25) was treated with alcoholic KOH (10%, 200 ml) at room temp with thorough shaking. It was diluted with water and the oil and the aqueous alkaline layers separated. The aqueous solution was extracted with ether to remove neutral matter, and then carefully acidified with dil HCl aq in the cold. The regenerated acid was taken up in ether, washed free of mineral acid and dried (Na_2SO_4). On removal of ether a residue (75 g) was obtained. This acidic material was again dissolved in ether and extracted thoroughly with 10% $NaHCO_3$ aq. The ether solution was then extracted with 10% Na_2CO_3 aq. The $NaHCO_3$ and Na_2CO_3 extracts were kept separately. The remaining ether solution was preserved.

The Na_2CO_3 solution was extracted with ether to remove adhering neutral matter and then acidified with dil HCl aq. The liberated acid was extracted with ether and the ether solution washed free of mineral acid and dried (Na_2SO_4). Evaporation of ether gave the acid (29 g) as a dark, viscous liquid. It was dissolved in acetone (75 ml) and kept at −18° overnight when a solid separated; it was filtered and the mother liquor concentrated and left in a deep freeze cabinet for another 24 hr, when a small amount of solid separated. The total amount of solid (2·5 g) was identified as a mixture of palmitic and behenic acids. When no further solid separated acetone was completely removed from the solution and crude acid (25 g) obtained.

The above acid (25 g) was dissolved in methyl ethyl ketone (200 ml) and treated with cyclohexylamine (12 g) and the mixture shaken vigorously. The cyclohexylamine salt (23 g) which separated at room temp as a solid was filtered and crystallized thrice from methyl ethyl ketone, m.p. 180–182°. GLC at this stage of the methyl ester of the acid regenerated from the salt showed three peaks.

The acid (15 g) was regenerated from the cyclohexylamine salt by treatment with 5% NaOH aq and subsequent acidification. It was dissolved in acetone (75 ml) and treated with dicyclohexylamine (12 g) when a solid salt (19 g) was formed. This was filtered and crystallized twice from acetone, m.p. 91–92°. The acid was regenerated from the salt as before. The acid thus obtained solidified (10 g) and was crystallized from dilute alcohol to yield pure costic acid (8 g), m.p. 87–88°, $[\alpha]_D^{26}$ +23·42°, (*c*, 1·3), λ_{max} 210 mμ, ε 5,030; IR bands at (Fig. 1), 1706, 1629, 1613, 1393, 1366, 1312, 1292, 1267, 1245, 1221, 1193, 1140, 1126, 1088, 1042, 1029, 1000, 987, 961, 934, 882, 850, 831, 814, 793 cm^{-1}. (Found: C, 76·79; H, 9·31. Equiv. wt. 231. $C_{15}H_{22}O_2$ requires: C, 76·88; H, 9·46% Equiv. wt. 234·33.)

Methyl costate (Ia). Costic acid (1 g) was dissolved in ether (15 ml) and an ethereal solution of diazomethane (prepared from 1 g nitrosomethylurea) added. Excess reagent was destroyed by adding two drops of acetic acid. The ethereal solution was washed free of acetic acid and dried (Na_2SO_4). The oil obtained after removal of ether was distilled (0·9 g), b.p. 135° (bath)/0·3 mm, n_D^{30} 1·5062, $[\alpha]_D^{27}$ +30·71° (*c*, 3·0), λ_{max} 210 mμ, ε 5,624. GLC single peak; IR bands at: (Fig. 1), 1706, 1629, 1613, 1425, 1245, 1140, 1126, 1088, 1019, 1000, 987, 934, 882, 850, 814 cm^{-1}. (Found: C, 77·41; H, 9·79. $C_{16}H_{24}O_2$ requires: C, 77·37; H, 9·74%.)

Selenium dehydrogenation of costic acid. The acid (1 g) was heated with Se (1·5 g) at 280–290°

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[*] Partially delactonized costus root oil was prepared by stage-wise cooling of petroleum ether solution of the oil at 0° and −18° when most of the solid lactones crystallized out.[3] The oil obtained after this process was used for the present work.

in N_2 for 15 hr. The product was diluted with pet. ether (40–60°) and passed through a column of alumina (grade II, 10 g) and eluted with pet. ether (40–60°; 100 ml). On evaporation of the solvent a hydrocarbon (360 mg) was obtained. It was distilled over metallic Na to yield a pure hydrocarbon (215 mg), b.p. 140° (bath)/10 mm λ_{max} 280 mμ, ε 2143; and 228 mμ, ε 48,700.

s-Trinitrobenzene (0·25 g) was added to the alcoholic solution of the hydrocarbon (0·21 g). Yellow crystals separated, which after 3 crystallizations from MeOH melted at 107–108°, mixed m.p. with authentic sample of the TNB adduct of 1-methyl-7-ethylnaphthalene was undepressed. (Found N, 11·14. $C_{19}H_{17}O_6N_3$ requires: N, 10·96%.)

Conversion of methyl costate to costol (IIa). The methyl ester (Ia, 0·73 g), dissolved in dry ether (25 ml) was added to a stirred slurry of AlH_3 (prepared by adding 0·33 g anhydrous $AlCl_3$ to an ethereal suspension of 0·35 g LAH) at room temp. The stirring was continued for 45 min. The excess reagent was destroyed by careful addition of moist ether. The product was isolated in the customary manner and distilled (0·53 g), b.p. 150° (bath)/0·5 mm, n_D^{26} 1·5180; $[\alpha]_D^{27}$ +34·33° (*c*, 4·5); IR bands at: (Fig. 1), 3356, 3115, 1639, 1433, 1403, 1370, 1330, 1261, 1174, 1147, 1095, 1053, 1020, 985, 930, 889, 858, 833, 793 cm^{-1}. (Found: C, 81·79; H, 11·19. $C_{15}H_{24}O$ requires: C, 81·76; H, 10·98%.)

Costal (IV). Costol (IIa, 1 g) dissolved in acetone (20 ml) was oxidized with the requisite quantity of Jones chromic acid reagent at 0°. The reaction mixture was diluted with water and extracted with ether. The ether extract was washed free of H_2SO_4 and with $NaHCO_3$ aq to remove any acid formed during oxidation. The ether solution was dried (Na_2SO_4) and the ether evaporated when costal (0·7 g) was obtained. It was distilled 130° (bath)/0·8 mm, n_D^{27} 1·4990; λ_{max} 216 mμ, ε 17,240. IR bands at: 2703, 1689, 1639, 1621, 1433, 1404, 1389, 1242, 939, 910, 886 cm^{-1}. (Found: C, 82·96; H, 10·53. $C_{15}H_{22}O$ requires: C, 82·51; H, 10·16%.)

Semicarbazone of costal. To costal (0·5 g) in alcohol (5 ml) was added an aqueous solution of semicarbazide hydrochloride (0·25 g) and sodium acetate (0·3 g). The semicarbazone formed was crystallized twice from EtOH, m.p. 223°, λ_{max} 262 mμ, ε 26,530. (Found: C, 69·78; H, 9·15; N, 15·26. $C_{16}H_{25}N_3O$ requires: C, 70·04; H, 9·19; N, 15·31%.)

Conversion of costol (IIa) *into β-selinene* (V). Metallic Li (0·5 g) was added in small lots to liquid ammonia (500 ml) under stirring. Costol (0·64 g) dissolved in dry tetrahydrofuran (150 ml) was then added dropwise during 30 min to the Li–ammonia complex. Stirring was continued for 3 hr after the addition was complete. The reaction mixture was allowed to stand at room temp overnight when most of the ammonia escaped. The residue was carefully diluted with water and extracted with ether. The ether solution was washed twice with water and dried (Na_2SO_4). The product obtained after removal of ether was passed through a column of neutral alumina (grade I, 10 g) and eluted with pet. ether (40–60°). On removal of the solvent 0·6 g material was obtained, b.p. 140° (bath)/7 mm, n_D^{29} 1·4900, $[\alpha]_D^{30}$ +59·51° (*c*, 2·05). IR bands at: (Fig. 1), 3086, 1637, 1429, 1395, 1368, 1253, 1167, 1140, 1042, 1012, 980, 952, 930, 885, 854 cm^{-1}. (Found: C, 88·3; H, 11·76. $C_{15}H_{24}$ requires: C, 88·16; H, 11·84%.)

Conversion of costol (IIa) *into selinane* (VI). Costol (0·26 g) dissolved in EtOH (15 ml) was catalytically hydrogenated in presence of Pd—C (5%, 0·25 g). Hydrogenation was stopped when absorption of H_2 stopped. The product was worked up as usual and passed through neutral alumina (grade II; 15 g) and eluted with pet. ether (40–60°). On removing the solvent 0·15 g hydrocarbon was obtained. It was distilled over metallic Na, b.p. 150° (bath)/7 mm. It was identified as selinane by GLC analysis, and IR spectra.

Ozonization of methyl costate. Methyl costate (0·78 g) was dissolved in glacial acetic acid (20 ml) and ozonized O_2 was passed through it at room temp for 3 hr. The ozonide was left at room temp for 2 hr. 2 N HCl (20 ml) was added followed by glacial acetic acid (15 ml) to make the solution clear. The solution was allowed to stand overnight at room temp. The solvent was evaporated under red. press. and the residue taken up in ether. The ether solution was washed with water and then extracted with 10% Na_2CO_3 aq (25 ml). The aqueous alkaline solution was acidified with dil HCl. The bulk was saturated with NH_4Cl and thoroughly extracted with ether. Removal of ether gave VII (0·71 g). It was esterified with diazomethane and the methyl ester distilled (0·3 g), b.p. 145° (bath)/0·08 mm.

Semicarbazone of the above methyl ester (0·3 g) was prepared from semicarbazide hydrochloride (0·17 g) and sodium acetate (0·2 g). The semicarbazone, after 3 crystallizations from EtOH melted at 236°. (Found: C, 60·01; H, 7·69; N, 15·22. $C_{14}H_{23}O_3N_3$ requires: C, 59·76; H, 8·24; N, 14·94%.)

Tetrahydrocostic acid (VIII). Costic acid (0·1987 g) dissolved in EtOH (8 ml) was hydrogenated in presence of Pd—C (5%, 0·05 g). Total H_2 absorption was 44·8 ml at 24° and 713 mm corresponding to two double bonds. The product was isolated in the customary manner.

Methyl ester. The tetrahydro acid (0·19 g) was esterified with diazomethane and the methyl ester thus formed was distilled (0·15 g), b.p. 135° (bath)/0·7 mm, n_D^{28} 1·4849; $[\alpha]_D^{27}$ +24·88° (*c*, 2·7), λ_{max} 210 mμ, ε 728, IR bands at: 1727, 1445, 1376, 1348, 1250, 1227, 1190, 1149, 1099, 1060, 1026, 985, 847 cm^{-1}. (Found: C, 76·35; H, 11·28. $C_{16}H_{28}O_2$ requires: C, 76·14; H, 11·18%.)

Conversion of costic acid into dihydroeudesmol (XIII). Tetrahydrocostic acid (1·2 g) was added at 0° to a solution of Me Li (prepared from 0·5 g Li and 5 g MeI) in dry ether during 10 min. The reaction mixture was stirred at room temp for ½ hr after the addition. Excess reagent was carefully destroyed by addition of moist ether, followed by water. Aqueous and ethereal layers were separated. The ether layer was washed with water and dried (Na_2SO_4). On removal of ether an oil was obtained (1·0 g). It was chromatographed on neutral alumina (grade II, 20 g) and eluted with pet. ether (40–60°). Removal of solvent gave the methyl ketone (IX, 0·86 g). IR bands at : 1704, 1381, 1366, 1220, 1155, 1109, 975, 943 and 866 cm^{-1}. The methyl ketone (0·86 g) was dissolved in $CHCl_3$ (20 ml) and 0·2 N perbenzoic acid (20 ml) and toluene-*p*-sulphonic acid (0·05 g) were added. The mixture was stirred at room temp for 40 hr. The $CHCl_3$ solution was washed with water, Na_2CO_3 aq and water again and dried (Na_2SO_4). The product obtained on removing $CHCl_3$ was passed through neutral alumina (grade II, 10 g) and eluted with pet. ether (40–60°). Removal of solvent gave X (0·72 g). The acetate was saponified with 10% alcoholic KOH (20 ml) for 3 hr. The reaction was worked up as usual and the neutral material was isolated as a thick oil. It was chromatographed on a column of neutral alumina (grade II, 15 g) and eluted with pet. ether and ether (80 ml). The ether fraction yielded XI (0·58 g).

The alcohol (0·58 g) was oxidized in acetone solution with Jones' chromic acid reagent. The product was isolated as usual and chromatographed on neutral alumina (grade II, 10 g) and eluted with pet. ether (40–60°). Removal of solvent gave XII, b.p. 140°(bath)/1 mm, n_D^{27} 1·4870; $[\alpha]_D^{27}$ −2·0° (*c*, 4·7). IR bands at: 1709, 1449, 1379, 1351, 1238, 1156, 1018, 975 cm^{-1}. (Found: C, 80·67; H, 11·68. $C_{14}H_{24}O$ requires: C, 80·71; H, 11·61%.)

Semicarbazone of (XII). The C_{14}-ketone (0·1 g) was converted into its semicarbazone with semicarbazide hydrochloride (0·05 g) and sodium acetate (0·055 g). The product was crystallized from EtOH, m.p. 206–207°. (Found: N, 15·64. $C_{15}H_{27}ON_3$ requires: N, 15·8%.)

Dihydroeudesmol (XIII). The ketone (0·2 g) dissolved in dry ether (10 ml) was added at 0° under stirring to a solution of MeMgI (prepared from 0·2 g Mg wire and 3 g MeI) in dry ether. The reaction mixture was stirred for 1 hr at 0° and was then poured into an ice-cold saturated solution (25 ml) of NH_4Cl. The mixture was allowed to come to room temp and the organic layer separated. The aqueous layer was extracted twice with ether and the ether extract mixed with the original ether solution. It was dried (Na_2SO_4) and the ether evaporated when a solid (0·2 g) was obtained. It was sublimed at 75°/0·6 mm. The sublimate, m.p. 70–73°, was crystallized from pet. ether (60–80°) to give pure dihydroeudesmol, m.p. 83–85°; mixed m.p. with authentic sample was undepressed; $[\alpha]_D^{27}$ +15·09° (*c*, 2·7). Authentic sample of dihydroeudesmol had $[\alpha]_D^{27}$ +17·18° (*c*, 1·9). IR bands at: (Fig. 1) 3390, 1466, 1379, 1205, 1175, 1124, 985, 961, 921, 909, 854 cm^{-1}. (Found: C, 80·24; H, 12·60. $C_{15}H_{28}O$ requires: C, 80·29; H, 12·58%.)

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