CHEMISTRY OF THE NATURAL ORDER CUPRESSALES-41

THE STRUCTURE AND STEREOCHEMISTRY OF COMMUNIC ACID*

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(Received 17 May 1961)

Abstract—A new diterpene acid, communic acid, has been isolated as its sodium salt from the bark of the common juniper, Juniperus communis L. The structure and configuration (1a) of this acid follows from direct correlations with torulosol and with agathene dicarboxylic acid as well as from the results of degradation experiments.

SEVERAL compounds belonging to the diterpene group have recently been isolated from the heartwood of Juniperus communis L^{1-4} The steam volatile oil from the bark of the same species was first studied by Mattson.⁵ During a recent reinvestigation of the bark, carried out in this laboratory, a number of monoterpenes⁶ as well as sesquiterpenes, eg. longifolene and juniperol,^{7,8} were isolated. We have now examined the non-volatile acid components of the bark.

The chloroform extract of the bark is partly soluble in light petroleum. By shaking the latter solution with sodium hydroxide the sparingly soluble sodium salt of a new diterpene acid, communic acid, C20H29O2Na·H2O separates. The structure and configuration Ia is proposed for this acid.

Communic acid is very sensitive to acids and polymerizes on keeping and has not been obtained in a crystalline form.⁹ It is converted with diazomethane into the crystalline methyl ester (Ib), C₂₁H₃₂O₂, m.p. 105-106°. The ultra-violet spectrum of the methyl ester shows the presence of two conjugated double bonds and the compound gives an adduct with maleic anhydride. The infra-red spectrum of methyl communate indicates the presence of at least one exocyclic methylene group which is also present in the maleic anhydride adduct.

The mass spectrum of methyl communate indicates that communic acid is a bicyclic diterpene acid and the presence of a strong peak at m/e 181, (C₁₁H₁₇O₂), shown to originate from ring A in similar compounds by rupture of the C(6)-C(7)and C(9)-C(10) bonds and removal of hydrogen,¹⁰ is in accord with structure Ib.

² J. B. Bredenberg and J. Gripenberg, Acta Chem. Scand. 10, 511 (1956). ³ J. B. Bredenberg, Acta Chem. Scand. 11, 933 (1957).

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¹⁰ C. Enzell, Acta Chem. Scand. in press.

Preliminary communication. Ref. 9.

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Catalytic hydrogenations of sodium communate under different conditions followed by acidification furnishes di-, tetra- and hexa-hydrocommunic acid (IIa, III, IV). They are all oils, the tetra- and hexa-hydroderivatives probably being mixtures of stereo-isomers. Only the dihydroderivative shows an infra-red absorption attributable to the presence of an unsymmetrically disubstituted double bond. None of the hydrogenated acids exhibit any ultra-violet absorption characteristics of a conjugated diene. The formation of the fully saturated hexahydroderivative proves that communic acid is bicyclic.

Ozonolysis of methyl communate affords a crystalline keto-acid (Va). C₁₈H₂₄O₅, m.p. $171-172^{\circ}$, and formaldehyde in an amount corresponding to the presence of two terminal methylene groups. Methyl dihydrocommunate (IIb), gives the same degradation products and, in addition, methyl ethyl ketone which accounts for all the carbon atoms present. The tetrahydrocommunic acid preparation also affords methyl ethyl ketone on ozonolysis together with an amorphous dicarboxylic acid. These results can be explained on the basis of structure Ia for communic acid, IIa for dihydro- and III for tetrahydrocommunic acid.

The keto-acid (Va) seems to be identical with a compound, m.p. 171-172°, obtained by Ruzicka et al.¹¹ from agathene dicarboxylic acid. (Methyl esters both b.p. 165°/ 0.1 mm). No direct comparison, however, could be made. The formation of the keto-acid (Va) from agathene dicarboxylic acid may be due to an abnormal course of ozonization or, perhaps more likely, to the presence of 10-20 per cent of a β_{γ} -unsaturated isomer in the agathene dicarboxylic acid preparation of the Swiss authors.

Reduction of the keto-acid (Va) with potassium borohydride affords a γ -lactone (VI), C₁₆H₂₄O₄ which is stable to hydrogen bromide and therefore should be the cis-lactone.¹² (For similar compounds and reactions compare ref. $^{13-15}$). Reduction of the keto-acid (Va) or the lactone (VI) with lithium aluminium hydride gives the triol (VII).

When methyl communate (Ib) is reduced with lithium aluminium hydride a liquid alcohol, communol (VIII) C₂₀H₃₂O is obtained which is characterized as its 3,5-dinitrobenzoate (m.p. 115-117°) and as its maleic anhydride adduct. Reduction of communol with sodium in propanol affords isodihydrocommunol (IX), C₂₀H₃₄O, due to 1: 4-addition. This liquid alcohol forms a liquid acetate and is characterized as its 3,5-dinitrobenzoate (m.p. 107-108°). Isodihydrocommunol acetate on ozonolysis furnishes a crystalline acetoxy-diketone (X), C₁₉H₃₀O₄, m.p. 112·5-113·5°, in very good yield as well as formaldehyde and acetaldehyde, isolated as their 2,4-dinitrophenyl hydrazones.

The evidence so far adduced strongly suggests that communic acid contains a side-chain, possessing the structure -CH2-CH=C(CH3)-CH=CH2 and the formation of a γ -lactone (VI) indicates that the side-chain is attached to the rest of the molecule at a carbon atom next to an exocyclic double bond.

Communic acid is related to torulosol¹⁶ (XI) by the following reactions. Torulosol is dehydrated with a mixture of acetic acid and acetic anhydride to the trienol (XII)¹⁷

¹⁵ E. Lederer and D. Mercier, *Experientia* 3, 188 (1947).

17 C. Enzell, Acta Chem. Scand. in press.

¹¹ L. Ruzicka, E. Bernold and A. Tallichet, Helv. Chem. Acta 24, 223 (1941).

 ¹⁴ R. P. Linstead, Ann. Rep. Chem. Soc. 32, 13 (1935).
¹³ P. K. Grant and R. Hodges, Tetrahedron 9, 261 (1960).

¹⁴ L. Ruzicka and M. M. Janot, Helv. Chim. Acta 14, 645 (1931).

¹⁶ C. Enzell and S. R. Barreto, Acta Chem. Scand. in press.

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 $(\lambda_{\max} 227 \text{ m}\mu \text{ Methyl communate } \lambda_{\max} 232 \text{ m}\mu)$ which on reduction with sodium in propanol furnishes the dienol, (IX), the 3,5-dinitrobenzoate of which is identical with the corresponding derivative of isodihydrocommunol. These results establish the structure of communic acid as well as the configurations at C₅, C₉ and C₁₀ since torulosol has been related to manool of known configurations at these centres.¹⁷

Communic acid is also related to agathene dicarboxylic acid as follows: Dimethyl agathene dicarboxylate is reduced with lithium aluminium hydride to agathadienediol (XIII), the diacetate of which is ozonized to give the acetoxydiketone (X) (mixed m.p., identical I.R. spectra of the diketones as well as their 2,4-dinitrophenyl hydrazones). When agathadienediol (XIII) is oxidized with manganese dioxide, an α,β -unsaturated aldehyde (XIV) is obtained and on thermal isomerization¹⁸ yields the β,γ -unsaturated aldehyde. Ozonization of this substance, which would be analogous to the presumed impurity in the agathene dicarboxylic acid preparation ozonized by Ruzicka *et al.*, yields an hydroxy-keto-acid which is reduced to the triol (VII).

The configurations at all the asymmetric centres in communic acid follows from these interrelations. The configuration at C_6 in agathene dicarboxylic acid has been uncertain but it has recently been determined by interrelation with manool via torulosol.¹⁷ The steric arrangement of the hydrogen atoms at the trisubstituted double bond remains to be determined.

Methyl communate is recovered largely unchanged after boiling with methanolic potassium hydroxide solution (0.5 N) for two hours in agreement with the axial orientation of the carboxyl group at C_4 .¹⁹ The hydrogenated communic acids are ¹⁸ G. Ohloff, *Tetrahedron Letters* No. 11, 10 (1960).

¹⁹ F. E. King, D. H. Godson and T. J. King, J. Chem. Soc. 4102 (1954).

weaker^{20,21} than similar acids possessing equatorial carboxyl groups as shown in Table 1 which also contains the pK_{MCS}^* values for some diterpene acids which have not been included in earlier investigations.^{22,23}

Compound	pK [*] _{MCS}	Reference
1. Axial carboxyl group		· · · · · · · · · · · · · · · · · · ·
Agathene dicarboxylic acid		
C_{15} -methyl ester	8.50	24
Vouacapenic acid	8.52	24
Dihydrocommunic acid	8.65	Present work
Tetrahydrocommunic acid	8.65	Present work
Hexahydrocommunic acid	8.61	Present work
2. Equatorial carboxyl group		
Abietic acid	7.93	24
Dehydroabietic acid	7.90	24
Levopimaric acid	7.90	24
Neoabietic acid	7.91	24
Sandaracopimaric acid	7.92	25
(-Cryptopimaric acid)		

TABLE 1.	Apparent	DISSOCIATION	CONSTANT	(pK_{MCS}^*) OF	SOME	
DITERPENE ACIDS						

EXPERIMENTAL

Melting and boiling points are not corrected. Optical rotations were determined in chloroform and ultra-violet spectra in 95% ethanol, unless otherwise stated. Light petroleum refers to the fraction b.p. 40-60°. Small scale distillations were carried out in gradient sublimation tubes between 0.1 to 0.01 mm.

Isolation of sodium communate

Air dry bark of Juniperus communis L. (25 kg) was milled and extracted with chloroform for 8 hr in a Soxhlet extractor and the chloroform evaporated to give a thick concentrate (21.). Most of the chloroform from this concentrate (400 ml) was removed in vacuo and the red-brown residue (200 g) mixed with ether (85 ml). The mixture was poured into light petroleum (1.6 l) with constant stirring when a brown powder was precipitated. The greenish yellow solution was extracted once with sodium bicarbonate (10%, 400 ml). Sodium hydroxide solution (2 N, 750 ml) was then added with strong stirring when, gradually, crystals of a sodium salt separated from the aqueous phase. The salt was collected and crystallized from hot water to give a product (26 g), m.p. 155-165°. Two recrystallizations from water and three from methanol-water gave pure sodium communate, m.p. 228-230°, $[\alpha]_{D} + 25^{\circ}$ (c, 1.93, MeOH). (Found: C, 70.5; H 9.05; Na 6.7; H₂O 5.55%). U.V. λ_{max} 233 m μ (e 20,000).

Methyl communate (Ib)

Crude sodium communate (25 g) was suspended in water (21.) and shaken with ether (11.). Hydrochloric acid (2 N, 100 ml) was added quickly with vigorous shaking. The organic phase was washed several times with water, dried over anhydrous sodium sulphate and an excess of diazomethane added. After 8 hr the solvent was removed by distillation and the brown crystalline product (24 g) was chromatographed in four 6 g batches on alumina (grade II, 200 g). Elution with benzenelight petroleum (1:1) gave methyl communate (18.6 g) which was recrystallized from methanol-ether,

⁸⁰ R. D. Stolow, J. Amer. Chem. Soc. 81, 5806 (1959).
⁸¹ J. F. J. Dippy, S. R. C. Hughes and J. W. Laxton, J. Chem. Soc. 4102 (1954).

- 22 W. Simon, Helv. Chim. Acta 41, 1835 (1958).
- ²³ P. F. Sommer, V. P. Arya and W. Simon, Tetrahedron Letters No. 20, 18 (1960).
- ²⁴ V. P. Ayra, P. F. Sommer and W. Simon, unpublished work.
- ²⁵ V. P. Arya, C. Enzell, H. Erdtman and R. Ryhage, Acta Chem. Scand. in press.

m.p. 105-106°, $[\alpha]_D$ +48° (c, 2). (Found: C, 79.5; H, 10.0; OCH₃, 9.9 and C—CH₃, 7.9. C₂₁H₃₂O₂ requires: C, 79.7; H, 10.2; OCH₃ 10.0%). U.V. λ_{max} 232 m μ (ε 25,500). I.R. (KBr) Peaks at 3125, 1625, 995 (CCl₄: 3110, 1615, 990)(—CH—CH₂), 1790, 890 (CCl₄: 1780, 886 (>C—CH₂), 1725 (CCl₄: 1720 cm⁻¹ (ester).

The compound gave a light brown colour with tetranitromethane in chloroform solution and consumed 1.20 moles of perphthalic acid in 24 hr and 2.1 moles in 7 days (ether, 4°). On titration with bromine in chloroform, 2.9 moles were consumed.

Maleic anhydride adduct of methyl communate

Methyl communate (100 mg) was dissolved in dry benzene (1 ml) containing maleic anhydride (31 mg). After 12 hr at room temp, the solvent was evaporated and the residue crystallized from acetone-water. Needles, m.p. 169–171°, $[\alpha]_D + 86^\circ$ (c, 1·43). (Found: C, 72·0; H, 8·2; OCH₃, 7·5. C₁₅H₃₄O₅ requires: C, 72·4; H, 8·3; OCH₃ 7·5%). U.V. λ_{max} 211 m μ (ϵ 3,000) and 235 m μ (ϵ 900). I.R. (KBr) Peaks at 1840, 1775 (anhydride, 1720 (ester) and 890, 1645 cm⁻¹ (>C=CH₂).

Dihydrocommunic acid (IIa)

Sodium communate (685 mg) in dry methanol (20 ml) was hydrogenated in the presence of a 10% palladium-on-charcoal catalyst (100 mg) until one mole of hydrogen had been absorbed. The filtered solution was diluted with water (100 ml) and acidified with dil hydrochloric acid solution (20 ml) and the suspension extracted with ether. The oil (595 mg) obtained was distilled twice. $n_{21}^{p_1} = 1.5261$, $[\alpha]_D \cdots 46^{\circ}$ (c, 1.8). (Found: C, 78.6; H, 10.7. $C_{20}H_{32}O_2$ requires: C, 78.9; H, 10.6%). U.V. λ_{max} 206 m μ (ε 5,500). I.R. (CCl₄) Peaks at 890, 1650 (>C=CH₂) 1695 cm⁻¹ (carboxyl). The compound gave a yellow colour with tetranitromethane in chloroform, and consumed 1.95 moles of bromine.

Methyl dihydrocommunate (IIb)

Methyl communate (3·2 g) dissolved in ethanol (100 ml) was hydrogenated over a 5% palladium charcoal catalyst (0·6 g) until one mole of hydrogen had been absorbed. The filtered solution was evaporated and the residue distilled at about 148–149°/0·5 mm. $n_D^{33} = 1.5062$, $[\alpha]_D + 55^\circ$ (c, 1·9). (Found: C, 79·3; H, 10·6 and C—CH₂ 11·0. C₂₁H₂₄O₂ C, 79·2; H, 10·8%). U.V. λ_{max} 205 m μ (ε 8,140). I.R. (KBr) Peaks at 1720 (ester), 1645 and 885 cm⁻¹ (>C=CH₂). The compound consumed 1·94 moles of perphthalic acid (ether, 4°, 24 hr).

Tetrahydrocommunic acid (II)

Sodium communate (856 mg) in dry methanol (30 ml) was hydrogenated over a 10% palladiumcharcoal catalyst (220 mg) until two moles of hydrogen were absorbed. The oily product (730 mg) was isolated as above and distilled. $n_D^{32} = 1.5482$, $[\alpha]_D + 38^\circ$ (c, 2.4). (Found: C, 78.3; H, 10.95; O, 10.5. $C_{30}H_{34}O_3$ requires: C, 78.4; H, 11.2; O, 10.4%). No U.V. absorption above 210 m μ I.R. (CCl₄) Peaks at 1692 (carboxyl), 2980, 1384 cm⁻¹ (--CH₃).

Hexahydrocommunic acid (IV)

Sodium communate (342 mg) in dry methanol (10 ml) was hydrogenated over a platinum oxide catalyst (42 mg) until 3 moles of hydrogen had been absorbed and the oily acid (302 mg) was isolated as above and distilled. $n_D^{35} = 1.5364$, $[\alpha]_D + 45^\circ$ (c, 1.4). (Found: C, 77.7; H, 11.3 and C—CH₃ 12.2. $C_{20}H_{36}O_2$ requires: C, 77.9; H. 11.7%). No U.V. absorption above 210 m μ I.R. (CCl₄) Peaks at 1695 (carboxyl), 2990, 1385 cm⁻¹ (-CH₃). No colour reaction with tetranitromethane.

Ozonolysis of methyl communate

Methyl communate (575 mg) in methylene chloride (30 ml) was ozonized at -70° until a blue colour appeared. Water (100 ml) was added and the mixture boiled under reflux for 2 hr. After cooling the two layers were separated and the aqueous phase extracted with light petroleum. Formalde-hyde dimethone (400 mg) m.p. 191° was isolated from the aqueous phase on treatment with dimedone. (Yield: 1.4 moles of formaldehyde from one mole of methyl communate).

The mixed organic phases were separated into an acid fraction (a) and a neutral fraction (b). The acid fraction was crystallized from methanol giving colourless prisms of the *keto-acid* (5a; 48 mg),

m.p. $171-172^{\circ}$, $[\alpha]_{D} + 12^{\circ}$ (c, 1). (Found: C, 64.8; H, 7.9; OCH₃, 10.7. C₁₆H₂₄O₅ requires: C, 64.8; H, 8.2 and OCH₃, 10.5%). I.R. (in KBr) Peaks at 1724 (ester), 1702 (carbonyl) and 1695 cm⁻¹ (carboxyl).

The neutral fraction (b; 300 mg) refused to crystallize. It exhibited infra-red absorption at 3420 (weak, presence of small amounts of a compound containing a hydroxyl group), 2722 and 1715 cm⁻² (aldehyde). The product contained the aldehyde corresponding to the keto-acid (5a). In a second run methyl communate (2 g) was ozonized and methanol-water used for the decomposition of the ozonide. 1·3 g of acid (5a) and 0·4 g of the neutral product (b) were obtained.

Derivatives of the keto-acid (Va)

The keto-acid (50 mg) was esterified with diazomethane to give the oily *ester* (5b) which was distilled. $[\alpha]_D + 11.6^{\circ}$. (Found: C, 65.7; H, 8.5. $C_{1.7}H_{36}O_5$ requires: C, 65.8; H, 8.4%).

The keto-acid (Va) formed a *semicarbazone*. Crystals from methanol, m.p. 200-201°. (Found: C, 58.0; H, 7.8 and N, 11.7. $C_{17}H_{27}O_5N_3$ requires: C, 57.8; H, 7.7 and N, 11.9%).

The dimethyl ester (Vb) furnished a 2,4-*dinitrophenyl-hydrazone*. Yellow needles from methanol, m.p. 161-163°. (Found: C, 56·1; H, 6·4 and N, 11·7. $C_{23}H_{30}O_8N_4$ requires: C, 56·3; H, 6·2 and N, 11·4%).

The dimethyl ester (Vb) yielded a *semicarbazone*. Needles from aqueous methanol, m.p. 123-124°. (Found: C, 56.7; H, 8.1 and N, 10.6. $C_{1.8}H_{29}O_{5}N_{3}H_{2}O$ requires: C, 56.1; H, 8.1 and N, 10.6%).

Ozonolysis of methyl dihydrocommunate

Methyl dihydrocommunate (900 mg) in dry chloroform (30 ml) was ozonized at -70° until the appearance of a blue colour. Decomposition of the ozonide with water gave as volatile products, methyl ethyl ketone and formaldehyde isolated as their 2,4-dinitrophenylhydrazones by chromatography on alumina (grade II). The non-volatile fraction was separated into an acidic (230 mg) and a neutral fraction (365 mg). The acidic fraction crystallized from methanol. Needles m.p. 171°, identical with the keto-acid (Va). The neutral fraction did not crystallize.

Ozonolysis of tetrahydrocommunic acid

Tetrahydrocommunic acid (600 mg) in dry carbon tetrachloride (30 ml) was ozonized at -70° as above. Reductive decomposition with zinc dust (6 g) and glacial acetic acid (30 ml) furnished a non-volatile acid material (400 mg; Eq. wt. 139). This product refused to crystallize. The volatile product isolated from this experiment was methyl ethyl ketone, identified as the 2,4-dinitrophenylhydrazone.

Potassium borohydride reduction of the keto-acid (Va) to lactone (VI)

To the keto-acid (Va; 300 mg) in methanol (40 ml) and water (10 ml) potassium borohydride (200 mg) in sodium hydroxide solution (2 N, 3 ml) was added and the mixture left at room temp for 12 hr. On acidification with hydrochloric acid (2 N, 2 ml), crystals separated. The pure *lactone* (VI) was obtained by recrystallization from methanol-isopropyl ether, m.p. 163-164°, $[\alpha]_D - 10°$ (c, 1·6 MeOH). (Found: C, 68·8; H, 8·6. C₁₆H₂₄O₄ requires: C, 68·5; H, 8·6%). I.R. (in KBr) Peaks at 1775 (γ -lactone), 1715 cm⁻¹ (ester).

The lactone (VI) was recovered unchanged after boiling with 25% ethanolic hydrogen bromide. Lithium aluminium hydride reduction furnished the triol (VII).

Lithium aluminium hydride reduction of the keto-acid (Va) to the triol (VII)

The keto-acid (102 mg) in dry ether (50 ml) was reduced with lithium aluminium hydride (51 mg) for 4 hr at 35°. The reaction mixture was decomposed in the usual way and furnished a crystalline residue (51 mg). Crystals from methanol-ether, m.p. 218-220°, $[\alpha]_D 0°$ (c, 0.5, MeOH). (Found: C, 70.1; H, 10.8. C₁₈H₂₈O₃ requires: C. 70.3; H, 11.0%). I.R. (in KBr) Peaks at 3490, 3395, 3260, 1035 and 1015 cm⁻¹ (hydroxyls).

Lithium aluminium hydride reduction of the amorphous neutral ozonolysis product of methyl communate furnished the same triol.

Communol (VIII)

Methyl communate (250 mg) in dry ether (30 ml) was slowly added to a suspension of lithium

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aluminium hydride (125 mg) in dry ether (20 ml) and boiled under reflux for 4 hr. The unreacted hydride was decomposed and on evaporating the organic solution a colourless liquid (216 mg) was obtained. This was chromatographed over a short column of alumina (grade I, 6 g). Elution with benzene-light petroleum (1:1) gave a colourless viscous oil which was distilled. $n_D^{80} = 1.3742$, $[\alpha]_D + 18^\circ$ (c, 2). (Found: C, 83·1; H, 11·2. $C_{s0}H_{s1}O$ requires: C, 83·3; H, 11·2%). U.V. $\lambda_{max} 233 \text{ m}\mu$ (ε 22,460). I.R. (in CCl₄) Peaks at 3560 (hydroxyl), 3100, 1605, 995 (--CH=-CH₃), 1790, 890 (conjugated double bonds), 1645 cm⁻¹ (>C=-CH₃).

The compound exhibited a brown colour reaction with tetranitromethane in chloroform.

Communol 3,5-dinitrobenzoate

A solution of communol (135 mg) in dry pyridine (2 ml) was left with 3,5-dinitrobenzoyl chloride at room temp for 24 hr. The resulting red-orange oil (169 mg) was purified by chromatography on a short column of alumina (grade II, 15 g). Elution with light petroleum-benzene (4:1) gave a product, m.p. 110°. Needles from methanol-ether, m.p. 115-117°, $[\alpha]_D + 7^\circ$. (Found: C, 67·4; H, 7·1 and N, 6·1. C₂₇H₃₄O₆N₂ requires: C, 67·2; H, 7·1; N, 5·8%). U.V. λ_{max} 232 m μ (ϵ 30,200).

Maleic anhydride adduct of communol

Communol (110 mg) in dry benzene (1 ml) was allowed to react with maleic anhydride (31 mg) at room temp for 24 hr. The solvent was evaporated and the residue (120 mg) was first crystallized from acetone-isopropyl ether and later 4 times from acetone-light petroleum. Needles, m.p.185-187°, $[\alpha]_D + 49^\circ$ (c, 2). (Found: C, 74·1; H, 8·8. C₂₄H₃₄O₄ requires: C, 74·5; H, 8·9%). U.V. λ_{max} 237 m μ (ε 1·680). I.R. (KBr) Peaks at 3460 (hydroxyl), 1845, 1750 (anhydride), and 886, 1645 cm⁻¹ (>C=CH₃).

Isodihydrommunol (IX)

To communol (2.8g) in absolute propanol (45 ml) sodium (3 g) was added in portions during 2 hr. The reaction mixture was poured into cold hydrochloric acid (2 N, 500 ml) and extracted with ether. The ether extract was washed and gave a liquid (2.5 g) which was distilled. $n_D^{00} = 1.3628$, $[\alpha]_D + 21^{\circ}$ (c, 3). (Found: C, 82.6; H, 11.5 and C—CH₃ 11.4. C₂₀H₃₄O requires: C, 82.7; H, 11.8%). U.V. λ_{max} 208 mµ (ε 3,470). I.R. (CCl₄) Peaks at 3570 (hydroxyl) and 886, 1647 cm⁻¹ (>C=CH₂).

Isodihydrocommunol 3,5-dinitrobenzoate

Isodihydrocommunol (1 g) was heated with 3,5-dinitrobenzoyl chloride (1 g) in dry pyridine (10 ml) on the steam bath for 10 min. After 12 hr at room temp, the ester (1.6 g) was isolated. Repeated crystallizations from methanol-ether gave crystals, m.p. $107-108^{\circ}$, $[\alpha]_{\rm D}$ +9° (c, 3.9). (Found: C, 66.7; H, 7.4; N, 5.9. C₂₇H₃₆O₆N₃ requires: C, 66.9; H, 7.5; N, 5.8%).

Isodihydrocommunol acetate

Isodihydrocommunol (900 mg) was acetylated (Ac₄O, pyridine, room temp 36 hr). The oil (912 mg) obtained was distilled. $[\alpha]_D + 16^\circ$. (Found: C, 79.0; H, 10.7 and --COCH₃ 12.6. C₂₂H₃₆O₂ requires: C, 79.4; H, 10.9 and --COCH₃ 13.0%). I.R. (CCl₄) Peaks at 1740, 1240 (acetate), 890, 1655 cm⁻¹ (>C--CH₂). No hydroxyl band.

Ozonolysis of isodihydrocommunol acetate

Isodihydrocommunol acetate (800 mg) in methylene chloride (30 ml) was ozonized as usual at -70° . Glacial acetic acid (30 ml) and zinc dust (10 g) were added and the mixture shaken for 2 hr. The filtered solution was diluted with water (300 ml) and the resulting suspension was vigorously shaken for 15 min. The methylene chloride layer was separated from the aqueous phase which was extracted twice with methylene chloride (20 ml). Aqueous solution (A).

The methylene chloride extracts were combined and the solvent partly distilled into a solution of 2,4-dinitrophenyl-hydrazine hydrochloride in methanol (B; see below). The residue remaining after removal of methylene chloride crystallized from ether light petroleum on cooling to -60° (600 mg), m.p. 111-112.5°. Several recrystallizations from the same solvent gave the pure *acetoxydiketone* (10), m.p. 112.5-113°, $[\alpha]_{\rm D}$ +29.6° (c, 1.48). (Found: C, 70.4; H, 9.2; O, 19.85 and -COCH₃, 13.55. C₁₉H₃₀O₄ requires: C, 70.8; H, 9.4; O, 19.8 and -COCH₃, 13.4%). U.V. $\lambda_{\rm max}$ 282 m μ (ϵ 56). I.R. (CCl₄) Peaks at 1712 (carbonyl), 1740, 1240 cm⁻¹ (acetate).

The aqueous solution (A) was partly distilled into the solution (B) and the mixture boiled under reflux for 1 hr. On cooling a mixture of 2,4-dinitrophenylhydrazones separated (300 mg), m.p. 128-135°. It was dissolved in benzene-chloroform (1:1) and filtered through alumina (grade II, 15 g). The eluate (283 mg) was adsorbed on anhydrous magnesium sulphate (12 g) from benzene. Elution with benzene-chloroform (9:1) yielded acetaldehyde 2,4-dinitrophenylhydrazone (111 mg). Needles from dilute ethanol, m.p. and mix m.p. 168°. Further elution with benzene-chloroform (3:1) gave formaldehyde 2,4-dinitrophenylhydrazone (144 mg), m.p. and mix. m.p. 166°.

Bis-2,4-dinitrophenylhydrazone of acetoxydiketone (X), crystals from chloroform-methanol, m.p. 241-242°. (Found: C, 56.7; H, 5.7 and N, 17.0. $C_{31}H_{38}O_{10}N_8$ requires: C, 56, 5; H, 5.8 and N, 17.1%).

Methyl isodihydrocommunate

To methyl communate (4.6 g) in absolute ethanol (120 ml) sodium (22 g) was added during 2 hr. Heating was then continued for 1 hr. The mixture was cooled, diluted with water and extracted with ether. The ethereal extract gave an oil, which distilled at about $152-158^{\circ}/0.3$ mm, $[\alpha]_{D} + 45^{\circ}$ (c, 3.95). (Found: C, 79.2; H, 10.8. C₂₁H₃₄O₂ requires: C, 79.2; H, 10.8%). U.V. λ_{max} 208 m μ (ε 9.110). I.R. (KBr) Peaks at 1730 (ester), 1645 cm⁻¹ (>C=CH₂).

Isodihydrocommunol (X) from methylisodihydrocommunate

Methyl isodihydrocommunate (3 g) in dry ether (20 ml) was added to a suspension of lithium aluminium hydride (0.8 g) in dry ether (50 ml) and the mixture heated under reflux for 3 hr. The reaction product, an oil (2.5 g) was distilled at about $148^{\circ}/0.3$ mm. It furnished a 3,5-dinitrobenzoate, m.p. 107-108° alone or mixed with isodihydrocommunol 3,5-dinitrobenzoate. Identical I.R. curves. (Found: C, 66.6; H, 7.4 and N, 5.9. C₂₇H₂₆O₆N₂ requires: C, 66.9; H, 7.5 and N, 5.8%).

Dehydration of torulosol (XI) to the trienol (XII)

Torulosol (1 g) was dehydrated with acetic acid-acetic anhydride (1:1, 2.5 ml) as described by Enzell¹⁷ to give the oily trienol (12; 150 mg), (λ_{max} 227 m μ ; ε 22,000) which was converted into its 3,5-dinitrobenzoate, m.p. 73-74°, [α]_D +16° (c, 1.5). (Found: C, 67.5; H, 7.3 and N, 5.6. C₂₇H₃₄O₆N₂ requires: C, 67.2; H, 7.1 and N, 5.8%). I.R. (KBr) Peaks at 1725 (ester) and 886, 1645 (>C-CH₂) and 1630 cm⁻¹ (-CH=CH₂).

Reduction of trienol (12) to isodihydrocommunol (9)

To the trienol (250 mg) in propanol (10 ml), sodium (250 mg) was added during 2 hr. The oily reaction product was distilled to give a product, $[\alpha]_D + 20.5^\circ$ (c, 2), the infra-red spectrum of which was superimposable with that of isodihydrocommunol. The 3,5-dinitrobenzoate had m.p. 107-108° alone or when mixed with isodihydrocommunol 3,5-dinitrobenzoate derived from communic acid.

Monomethyl ester of agathene dicarboxylic acid

Esterification of the C₁₅-carboxyl group. Agathene dicarboxylic acid (100 mg) in anhydrous methanol (5 ml) and conc sulphuric acid (3 drops) was refluxed for 2 hr. The product was isolated in the usual manner and distilled. $n_{\rm D}^{33} = 1.4962$, $[\alpha]_{\rm D} + 61^{\circ}$ (c, 1). (Found: C, 72.4; H, 9.3. C₂₁H₂₂O₄ requires: C, 72.4; H, 9.3%). U.V. $\lambda_{\rm max}$ 220 m μ (ϵ 13,000). I.R. (CCl₄) Peaks at 1722 (ester), 1698 (carboxyl), 1652 (conjugated double bond), 890 cm⁻¹ (>C=CH₂).

The monomethyl ester was methylated with diazomethane to the dimethyl ester which after distillation had $n_D^{34} = 1.5129$, $[\alpha]_D + 63^\circ$ (c, 1) (Lit.²⁶ b.p. 196–198°/0.6 mm, $n_D^{17} = 1.5163$, $[\alpha]_D + 54.6$ to $+61.1^\circ$).

Agathadienediol (XIII)

Dimethyl agathene dicarboxylate (2 g) in dry ether (40 ml) was reduced with lithium aluminium hydride (1 g) in dry ether (100 ml) by boiling under reflux for 4 hr. The reaction mixture gave a gum (1.4 g) which crystallized from methanol-isopropyl ether, m.p. $107-108^{\circ}$ (Yield 1 g). (Lit.¹⁷ m.p. $107-108^{\circ}$).

²⁶ L. Ruzicka and J. K. Hosking, Liebigs Ann 469, 147 (1929).

Agathadienediol diacetate

Agathadienediol (2 g) was acetylated (pyridine and acetic anhydride) at room temp. The product obtained was a liquid which was twice distilled. $n_{23}^{23} = 1.5645$, $[\alpha]_D + 23^\circ$ (c, 2·2). (Found: C, 73·6; H, 9·85 and $-COCH_3$ 22·0. $C_{24}H_{28}O_4$ requires: C, 73·8; H, 9·8 and $-COCH_3$ 22·0%).

Ozonolysis of agathadienediol diacetate

Agathadienediol diacetate (900 mg) in methylene chloride (25 ml) was ozonized at -70° as usual. The gummy ozonide was dissolved in glacial acetic acid (20 ml) and shaken with zinc dust (8 g) for 15 min and then at intervals for 2 hr. Excess zinc was removed by filtration, the methylene chloride evaporated and water (200 ml) added. An ether extract yielded a neutral residue (660 mg). This was crystallized twice from ether-light petroleum, m.p. $112 \cdot 5 - 113^{\circ}$ alone or mixed with *acetoxydiketone* (X) prepared by ozonolysis of isodihydrocommunol acetate. The infra-red spectra were identical. The bis-2,4-dinitrophenylhydrazone, m.p. $241-242^{\circ}$ was also identical with the corresponding product from isodihydrocommunol acetate.

Manganese dioxide oxidation of agathadienediol to the aldehyde (XIV)

Agathadienediol (2 g) in dry acetone (300 ml) was stirred with manganese dioxide (30 g) at room temp for 15 hr. The solid material was washed with acetone and the combined acetone solutions were evaporated to dryness. The residue (1.7 g) on recrystallization from isopropyl ether gave crystals, m.p. 73-74°, $[\alpha]_D + 40°$ (c, 2) (Found: C, 78.9; H, 10.6. C₂₀H₃₂O₂ requires: C, 78.9; H, 10.9%). U.V. λ_{max} 239 m μ (ϵ 15,450).

The aldehyde (XIV) formed a 2,4-*dinitrophenylhydrazone*, orange-red needles from chloroformmethanol, m.p. 132-133° (Found: C, 64·2; H, 7·5; N, 11·6. $C_{26}H_{36}O_6N_2$ requires: C, 64·4; H, 7·3 and N, 11·5%).

Conversion of the aldehyde (XIV) to the triol (VII)

The α,β -unsaturated aldehyde (XIV; 1.8 g) was heated in a distillation apparatus (bath temp 140°/ 0.01 mm) when it slowly distilled (in about 12 hr). The distillate (1.63 g) refused to crystallize. On chromatography, a product was obtained which according to U.V. and I.R. data contained about 90% of a β,γ -unsaturated aldehyde and 10% of unchanged material. This product (1.1 g) was ozonized in the usual way and the ozonide decomposed with water. The acidic product (0.3 g) was reduced with lithium aluminium hydride in dry ether. The reduction product, crystals from methanol, m.p. 218– 220° was identical (mixed m.p. and I.R.) with the triol (VII).

Acknowledgements—We thank Professor and Mrs. N. A. Sörensen, Trondheim, for the crude chloroform extract of the juniper bark, Dr. C. Enzell for various starting materials and numerous discussions, Miss G. Hammarberg for the determination of infrared and ultraviolet absorption spectra, Dr. A. Wettstein, *Ciba Ltd.*, Basel, for several microanalytical data, Dr. W. Simon, E.T.H., Zürich, for measuring the apparent dissociation constants and Dr. P. Daniels for checking the language of the manuscript. We also acknowledge with gratitude the *Ciba Fellowship Trust*, Cambridge, for a postdoctoral fellowship to one of us (V. P. A.) and the U.S. Army and Development Liaison group for financial support (contract number DA-91-591-EUC-1113).