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The Chemistry of the Natural Order Cupressales *38* *

The Structures of the Diterpenes Torulosol, Torulosal and Agatholic Acid **

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Torulosol (*1*) and torulosal (*2*), occurring in *Cupressus torulosa*, have been correlated with manool and agathic acid and shown to be a hydroxy- and an oxo-manool, respectively.

Agatholic acid (*7*), isolated from Manila copal, has been correlated with the substances mentioned and prepared therefrom.

The mass-spectra of these and some related compounds are discussed.

Two new diterpenes, torulosol, $C_{20}H_{34}O_2$ (*1*) † and torulosal, $C_{20}H_{32}O_2$ (*2*), were isolated during a recent investigation of the heartwood constituents of *Cupressus torulosa* [1]. They occur in the heartwood in comparatively large amounts together with a number of other substances of which manool, from biogenetic and chemotaxonomic points of view, is perhaps the most interesting. The structures assigned to torulosol and torulosal are based on the following evidence.

Torulosol (*1*) on hydrogenation with a Raney-nickel catalyst gave dihydrotorulosol (*3*) and with a palladium catalyst tetrahydrotorulosol. This indicated that the compound was dicyclic since the two oxygen atoms were present as hydroxyl groups.

Oxidation of torulosol with chromium trioxide in pyridine gave torulosal (*2*), which had also been isolated from the wood of *Cupressus torulosa* [1]. The aldehyde group of torulosal, (1 716 and 2 720 cm^{-1}; −97 c/s from an internal benzene ref. at 40 Mc/s) did not react with silver oxide or Schiff's reagent and

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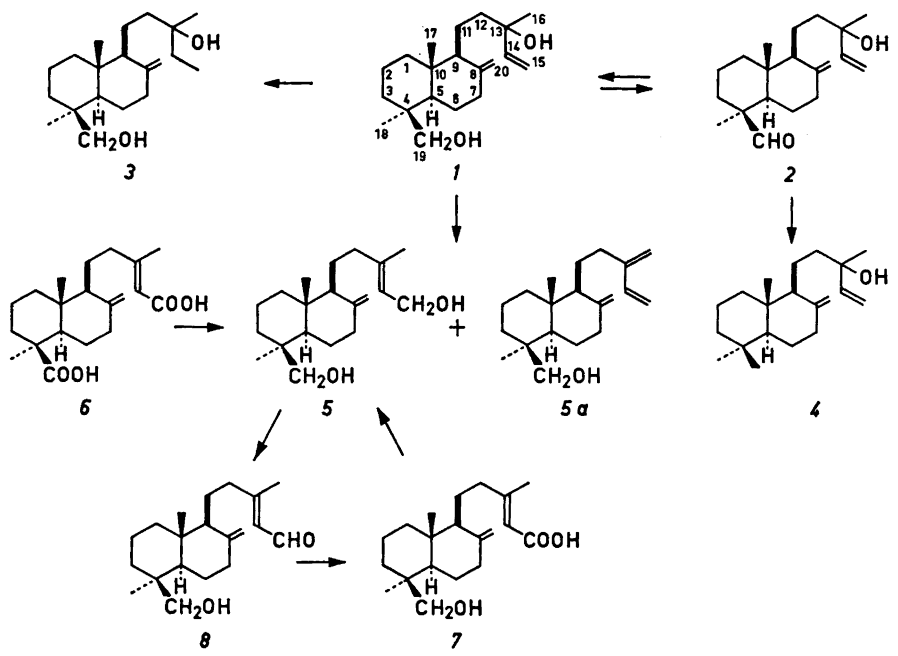
** The present names, being less confusing or shorter, are preferred to torulol, torulal and agathadienecarbinolcarboxylic acid, used when part of this work was presented at "De tredje kemistdagarna i organisk kemi", Stockholm 9–11 June 1960, *Svensk Kem. Tidskr.* **9** (1960) 602; the name agathadienecarbinolcarboxylic acid has been used once previously [14].

† Numbering system: Cocker, J. D and Halsall, T. G. *J. Chem. Soc.* **1956** 4262.



this was attributed to steric hindrance. It crystallised together with carbon-tetrachloride, possibly as an "inclusion compound" [2]. Torulosal, not being completely stable, is best characterised by conversion to torulosol with potassium borohydride or as the semicarbazone.

These results and a comparison of the infrared and mass spectra of manool and torulosol indicate that the latter is a hydroxy manool. The infrared spectrum of torulosol (Fig. 1) shows considerable similarity to that of manool and differs mainly in the presence of an additional hydroxyl band (1 020 cm^{-1}). The mass spectra of manool (Fig. 4) and torulosol (Fig. 5) show a series of strong peaks in common and a series of strong peaks differing by the

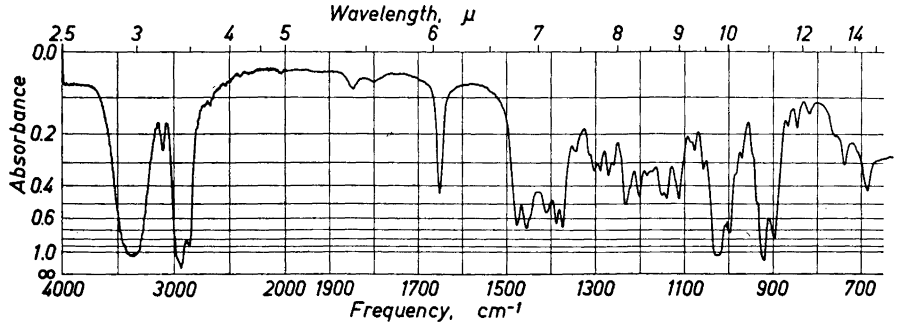


Fig. 1. Infra-red spectrum of torulosol (KBr).

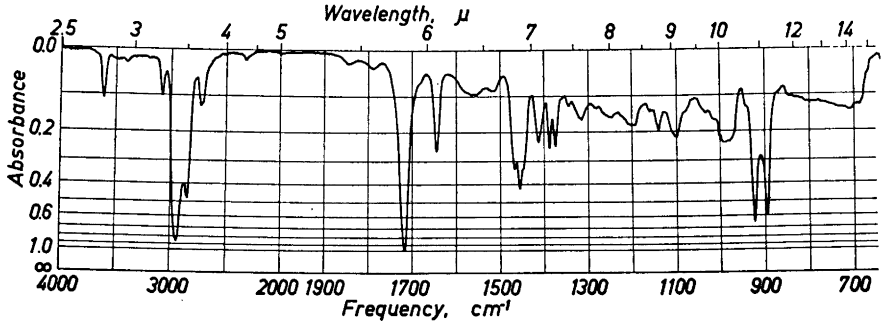


Fig. 2. Infra-red spectrum of torulosal (CCl_4).

atomic weight of oxygen. Of the peaks in common those at *m/e* 71 are probably due to the ion (CH_3—C(OH)—CH=CH_2) obtained by rupture of the C(12)—C(13) bond [3], since they occur at *m/e* 73 in the spectra of the dihydrocompounds, and indicate that these parts of the two compounds are identical. Further comparison indicates a common *A*,*B*-ringcarbon skeleton and that the primary carbinol group is located on ring *A*. The reasons for these conclusions are given below.

Huang-Minlon reduction of torulosal (*2*) gave manool (*4*), for which the structure and absolute configuration at C(5), C(9) and C(10) are known [4-6] and that at C(13) has been suggested [7]. This correlation therefore established the structure and stereochemistry at these centres of torulosal and torulosol except for the position of the extra oxygen atom.

The position of the extra oxygen atom was determined by subjecting torulosol to an allylic rearrangement [8,9] yielding, the triene alcohol (*5a*) and the diol (*5*). The latter was identical with a synthetic specimen obtained from the dimethyl ester of agathic acid (*6*) by lithium aluminium hydride reduction. Since the tertiary carboxyl group of agathic acid has been shown [10] to be in the 4*β*-position, it follows that torulosol (*1*) and torulosal (*2*) are oxygenated at C(19). The triene alcohol (*5a*) and its dihydroproduct, obtained on reduction with sodium in alcohol, were used to establish the structure of communic acid [11].

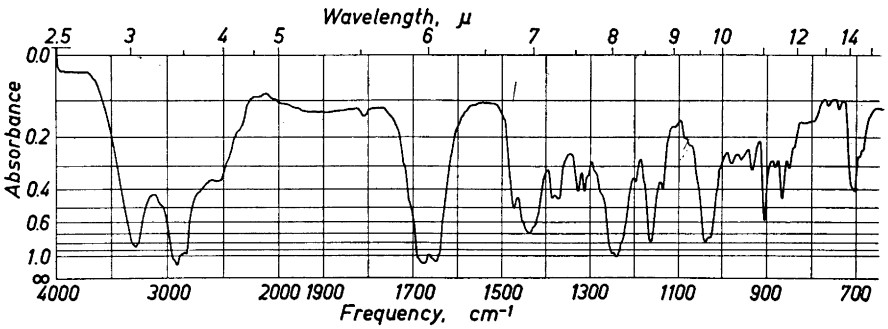


Fig. 3. Infra-red spectrum of agatholic acid (KBr).

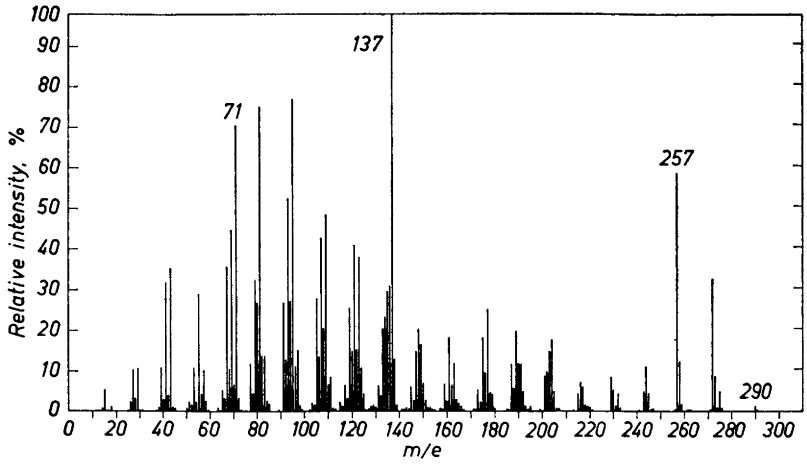


Fig. 4. Mass spectrum of manool.

The correlation of agathic acid (*6*) with manool (*4*) *via* torulosol proves that the side chain at C(9) is β-oriented in agathic acid.

The PMR spectrum of torulosol supports structure (*1*) and provides additional evidence for the β-orientation of the primary carbinol group. It showed, in addition to a C(4)-methyl band (254 c/s), an angular methyl band (268.5 c/s) and a side chain methyl band (244 c/s), a quartet (about 154 c/s) typical of an AB-spectrum [12] (J_{AB} 12 c/s). The position and splitting of this band suggest that it is due to the two non-equivalent methylene hydrogen atoms of the CH_2OH group. The most probable cause of non-equivalence of these two hyd-

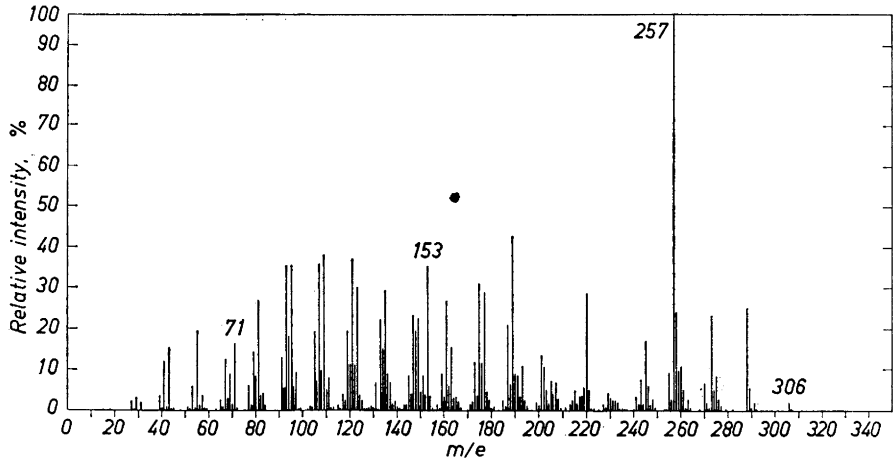
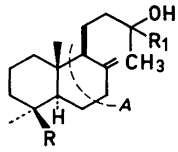
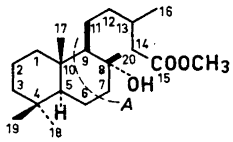


Fig. 5. Mass spectrum of torulosol.



9 (R CH_3; R_1 C_2H_5)
10 (R CDHOH; R_1 $CH{=}CH_2$)



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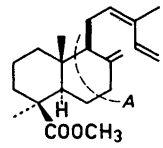

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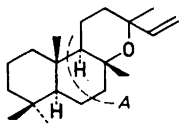

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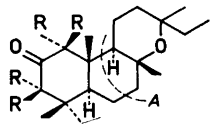
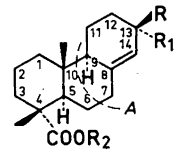
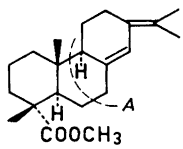


14 (R H)
15 (R D)



16 (R $CH{=}CH_2$; R_1 CH_3; R_2 CH_3)
17 (R $CH{=}CH_2$; R_1 CH_3; $R_2C_2H_5$)
18 (R CH_3; R_1 $CH{=}CH_2$; R_2 CH_3)



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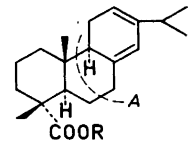

20 (R CH_3)
21 (R C_2H_5)

rogen atoms is restricted rotation of the group. Examination of molecular models indicates that this should only occur if the primary carbinol group is in the 4β-position where its rotation can be hindered by the 10β-angular methyl group.

Simultaneously with the isolation of agathic acid from a hard grade of Manila copal, attempts were also made to obtain this acid from a softer grade. The main product from this softer copal, when worked up largely according to the method given by Ruzicka and Hosking [13], was not agathic acid but a new acid, $C_{20}H_{32}O_3$, named agatholic acid. The infrared (Fig. 3), ultraviolet and mass spectra of this acid indicate that it is α,β-unsaturated and that it differs from torulosol only with respect to the side chain at C(9). Agatholic acid on esterification with diazomethane followed by reduction with lithium aluminium hydride gave the diol (*5*). This correlation together with the spectral data established the structure and absolute configuration of agatholic acid (*7*). The diol (*5*) on oxidation with manganese dioxide gave the hydroxy aldehyde (*8*) which on further oxidation with silver oxide gave agatholic acid.

The mass spectra of the new compounds and of several related known compounds show a point of interest. Peaks corresponding to ions obtained from ring *A* by rupture of the C(6)—C(7) and C(9)—C(10) bonds and removal of hydrogen — fragmentation A (see *9*, *etc.*) — were found to occur in the mass spectra of dicyclic as well as tricyclic diterpenes (*cf.* Table 1). In order to ascer-

Table 1. Peaks corresponding to fragmentations A in the mass spectra of some diterpenes. The figures within brackets give the peak intensities as percentages of the strongest peak in the spectrum.

Compound	Peaks corresponding to fragmentation A at *m/e*	
Manool (*4*)	137	(100)
Dihydromanool (*9*)	137	(100)
Torulosol (*1*)	153	(37)
Dihydrotorulosol (*3*)	153	(8)
Deuterotorulosol (*10*)	154	(13)
Torulosal (*2*)	151	(14)
Agatholic acid (*7*)	153	(24)
Methyl labdanolate * (*11*) [5]	137	(45)
Methyl communate (*12*) [11]	181	(15)
Manoyl oxide * (*13*) [15]	137	(43)
Dihydroketomanoyl oxide (*14*)	151	(20)
Deuterodihydroketomanoyl oxide (*15*)	155	(16)
Methyl pimarate (*16*) [16,17]	181	(24)
Ethyl pimarate (*17*) [17]	195	(11)
Methyl sandaracopimarate (*18*) [16,17,18]	181	(22)
Methyl neobietate (*19*) [17]	181	(10)
Methyl levopimarate (*20*) [17]	181	(17)
Ethyl levopimarate (*21*) [17]	195	(3)

tain the origin of these ions the mass spectra of deuterodihydroketomanoyl oxide [14] (*15*) and deuterotorulosol (*10*), prepared by reduction of torulosal with sodium and deuterium oxide in dioxan, were recorded. The peaks, corresponding to fragmentation A, were shifted in the expected manner.

The heights of the peaks resulting from fragmentation A were found to increase with the absence of polar substituents in ring *A* and with the presence at C(8) of a double bond exocyclic to ring *B* or of an 8 *a*-oxygen atom, which has been shown to be easily eliminated giving this double bond [6].

EXPERIMENTAL

Melting points were determined on a Kofler micro hot stage, unless stated to the contrary, and are corrected. Infrared spectra were recorded on a Perkin-Elmer No. 21 instrument (NaCl prism), ultraviolet spectra on a Beckman DK 2 recording spectro-photometer, mass spectra on an instrument [19] with an all glass heated inlet system (energy of electrons 70 eV) and PMR spectra (in $CDCl_3$; benzene internal standard) on a Varian V-4300 instrument operating at 40 Mc/s equiped with a Varian VK-3506 stabiliser. Microanalyses by Dr. A. Bernhardt, Mühlheim.

Torulosol (1) *and torulosal* (2) were isolated from the heartwood of *Cupressus torulosa* [1]: Torulosol, m.p. 110—111°, $[a]_D$ + 31° ($CHCl_3$, *c* 2.0), (Found: C 78.5; H 10.9; O 10.6. $C_{20}H_{34}O_2$ requires C 78.4; H 11.2; O 10.4 %). Torulosal, n_D^{25} 1.521, $[a]_D$ + 29° ($CHCl_3$, *c* 1.8), was not completely stable (about one half had changed on keeping in methanol solution for one week in stoppered pyrex tube at room temperature) and did not analyse well. (Found: C 78.4; H 10.2. $C_{20}H_{32}O_2$ requires C 78.9; H 10.6 %). It gave with carbon tetrachloride a compound, m.p. 80—85° (Pyrex tube), $[a]_D$ + 24° ($CHCl_3$, *c* 2.0), which even after drying (30°/0.001 mm) contained carbon tetrachloride (Found: C 59.4; H 7.7; O 12.9; Cl 19.6 %). The carbon tetrachloride was only partly removed on recrystallisation

* I am grateful to Professors S. Bergström and E. Stenhagen for allowing me to see these spectra prior to their publication.

from solvents such as methanol and *iso*propyl ether giving crystals of lower melting point and lower chlorine content (*e.g.*, after two recrystallisations from *iso*propylether followed by drying under high vacuum to constant weight. Found: C 72.8; H 9.6; Cl 6.5 %). Torulosal was characterised by conversion to torulosol or to the semicarbazone, m.p. 195—197° (decomp.), $[\alpha]_D$ −9° (pyridine, *c* 1.0), (Found: C 69.5; H 9.3; N 11.5. $C_{21}H_{35}O_2N_3$ requires C 69.8; H 9.8; N 11.6), which was prepared by a procedure used for O-methylpodocarpinal [20] and was purified by repeated recrystallisation from ethanol, chloroform and acetone.

The mass spectrum of torulosal includes major peaks at $m/e = 32$ (10), 49 (13), 55 (17), 57 (20), 61 (21), 69 (17), 71 (3), 85 (13), 89 (13), 99 (26), 100 (25), 111 (20), 125 (19), 135 (100), 137 (97), 151 (15; fragmentation A), 165 (13), 179 (13), 193 (10), 205 (11), 236 (13), 261 (11), 271 (6; loss of H_2O and CH_3), 275 (19; loss of CHO); 286 (5; loss of H_2O), 289 (10; loss of CH_3), 304 (10; molecular ion).

The figures within brackets give peak intensities as percentages of the strongest peak (135).

Tetrahydrotorulosol. Torulosol (150 mg, 0.49 mmole) was dissolved in ethanol (95 %, 15 ml) and hydrogenated over a pre-reduced palladium on charcoal catalyst (10 %, 20 mg) at room temperature and atmospheric pressure. It took up hydrogen in two steps; the first (11.6 ml) was completed in 20 min and the second (23.2 ml) in 30 hrs. The catalyst was filtered off, the solvent evaporated and the crystalline residue recrystallised from isopropyl ether and acetonitrile to give tetrahydrotorulosol, m.p. 119—124°, $[\alpha]_D$ + 16°, ($CHCl_3$, *c* 2.0), (Found: C 77.5; H 12.3; O 10.5. $C_{20}H_{38}O_2$ requires C 77.4; H 12.3; O 10.3 %).

Dihydrotorulosol (*3*). Torulosol (306 mg, 1 mmole) dissolved in absolute ethanol and in the presence of a Raney-nickel catalyst (50 mg) took up 0.9 mmole of hydrogen in 3 min whereafter the hydrogenation ceased. Filtration, evaporation of the solvent and recrystallisation of the crystalline residue from *iso*propyl ether and aqueous methanol followed by sublimation at reduced pressure gave dihydrotorulosol, m.p. 120—122°, $[\alpha]_D$ + 27° ($CHCl_3$, *c* 2.0) (Found: C 77.9; H 11.7. $C_{20}H_{36}O_2$ requires C 77.9; H 11.8 %) $\nu_{max}^{CCl_4}$ 3 660, 3 510, 1 127, 1 023; 3 100, 1 785, 1 648, 893 cm^{-1}.

When the hydrogenation, under the conditions described for tetrahydrotorulosol, was stopped after 1.1 mole of hydrogen per mole of torulosol had been consumed, the resulting material showed an infrared spectrum similar to that of torulosol, though the intensities of some bands (3110, 1847, 1651, 1410, 917, 894 cm^{-1}) were lower.

The mass spectrum of dihydrotorulosol (*3*) includes major peaks at m/e = 41 (87), 55 (100), 67 (55), 73 (35; $CH_3-C(OH)-CH_2CH_3$), 81 (83), 95 (48), 107 (25), 121 (19), 135 (16), 149 (11), 153 (8; fragmentation A), 161 (9), 177 (9), 189 (13), 203 (4), 220 (4), 243 (3), 259 (27; loss of CH_2OH and H_2O), 275 (7; loss of CH_3 and H_2O), 290 (4; loss of H_2O).

The figures within brackets give peak intensities as percentages of the strongest peak (55).

Chromium trioxide oxidation of torulosol. A solution of torulosol (500 mg) in pyridine (7 ml) was added to chromium trioxide-pyridine complex [21], prepared by adding chromium trioxide (500 mg) to pyridine (10 ml), and left 12 h at room temperature. Methanol (5 ml) was added and after an additional hour the reaction mixture was diluted with ice-cold aqueous sodium hydroxide (5 %, 100 ml) and extracted with ether. The ether solution was extracted with ice-cold hydrochloric acid (10 %) to remove pyridine, washed with water and dried (Na_2SO_4). The residue (430 mg), on recrystallisation from carbon tetrachloride, gave the torulosal-carbon tetrachloride compound, m.p. and mixed m.p. 80—85° (pyrex tube), $[\alpha]_D$ + 24° ($CHCl_3$, *c* 2.0). Infrared spectra identical. Semicarbazone, m.p. and mixed m.p. 195—197° (decomp.), $[\alpha]_D$ −11° (pyridine, *c* 1.5).

Potassium borohydride reduction of torulosal. Torulosal (200 mg), isolated from a heartwood extract of *Cupressus torulosa* [1], was added to a solution of potassium borohydride (200 mg) and sodium hydroxide (5 mg) in aqueous methanol (1:9, 10 ml) and left overnight. The reaction mixture was diluted with water (200 ml) and extracted with ether. The ether extract was dried (Na_2SO_4) and the solvent was removed to give a crystalline residue (170 mg), which on recrystallisation from *iso*propyl ether and sublimation gave pure torulosol, m.p. and mixed m.p. with the natural product 110—111°, $[\alpha]_D$ + 31° ($CHCl_3$, *c* 2.1). Infrared spectra identical.

Huang-Minlon reduction of torulosal. Crude torulosal (360 mg), obtained on oxidation of torulosol with chromium trioxide-pyridine complex, potassium hydroxide (550 mg) and hydrazine hydrate (99—110 %, 0.62 ml) in diethylene glycol (7 ml, redistilled) were refluxed for 1 h. The apparatus was changed to distillation and the internal temperature raised to 200° whereafter the mixture was refluxed (220—240°) under oxygen-free nitrogen for 4 h. The reaction product was diluted with water (50 ml) and extracted with light petroleum (b.p. 35—60°). The extract was dried (Na_2SO_4) and the solvent removed leaving an oil (310 mg) which was chromatographed on alumina (10 g, Merck stand., activity II). Light petroleum (b.p. 35—60°)-ether eluated an oil (260 mg), which immediately started to crystallise when seeded with manool. Recrystallisation from light petroleum gave pure manool (*4*), m.p. and mixed m.p. 53—55°, $[\alpha]_D$ + 33° ($CHCl_3$, *c* 1.2). Infrared spectrum identical with that of authentic material.

Torulosol, diethylene glycol (7 ml) and potassium hydroxide (550 mg) on refluxing under oxygen-free nitrogen for 4 h gave an almost quantitative yield of unchanged starting material, m.p. and mixed m.p. 110—111°, $[\alpha]_D$ + 31° ($CHCl_3$, *c* 1.3). Infra-red spectra identical.

Rearrangement[8] *of torulosol.* Torulosol (1.04 g) was boiled under reflux with a mixture of acetic anhydride (1.2 ml) and glacial acetic acid (1.2 ml) for 6 h. The reaction mixture was poured onto ice, made alkaline (10 % aq. NaOH) and extracted with ether. The ether solution was concentrated and the residue boiled under reflux with ethanolic potassium hydroxide (5 %, 15 ml) for 6 h. The reaction mixture was diluted with water (200 ml) and extracted with ether. The extract on drying (Na_2SO_4) and removal of the solvent gave a very thick oil (1.00 g), which was adsorbed on alumina (30 g; Merck neutral, activity II) and eluated with a light petroleum (b.p. 35—60°)-ether gradient.

The first fraction (0.46 g) was according to paper chromatographic results (hexadecane impregnated glass fibre paper and an aqueous methanol solution of silver fluoroborate as mobile phase)[22] and its ultra-violet absorption, λ_{max}^{EtOH} 227 mμ (ε 22 000), a mixture of a tricyclic compound and the triene alcohol (*5a*). The triene alcohol (*5a*), 3,5-dinitrobenzoate m.p. 71—72°, and its dihydroderivate, 3,5-dinitrobenzoate m.p. 105—106°, obtained on reduction with sodium and propanol, are discussed elsewhere[14]. The second fraction (0.40 g) was crystalline and recrystallisation from *iso*propyl ether gave pure agathadiol (*5*), m.p. 107—108°, $[\alpha]_D$ + 31° ($CHCl_3$, *c* 2.0). The mixed m.p. with the corresponding synthetic specimen from agathic acid dimethyl ester was undepressed, 107—108°. The infrared spectra of the two compounds were superimposable.

Agathic acid (*6*), m.p. 202—203°, $[\alpha]_D$ + 58° (EtOH, *c* 2.0), λ_{max}^{EtOH} 207 mμ (ε 12 000), 216 (ε 11 000), isolated from a hard grade of Manila copal (m.p. 135°) by a method described by Ruzicka and Hosking[12], gave on treatment with diazomethane followed by filtration through alumina (Merck, neutral, activity III) and quick distillation at low pressure (0.5 mm) agathic acid dimethyl ester, $[\alpha]_D$ + 63° (EtOH, *c* 2.0), n_D^{25} 1.5139, λ_{max}^{EtOH} 220 mμ (ε 13 000).

Agathadiol (*5*). Agathic acid dimethyl ester (1.1 g) dissolved in dry ether (7 ml) was added to a suspension of lithium aluminium hydride in dry ether (20 ml) and the mixture boiled under reflux for 6 h. Addition of ethyl acetate followed by icecold dilute sulphuric acid (5 %, 100 ml) and extraction with ether gave on evaporation of the solvent a crystalline residue (1.0 g), which was recrystallised from *iso*propyl ether-methanol to give pure agathadiol, m.p. 107—108°, $[\alpha]_D$ + 31° ($CHCl_3$, *c* 2.0) ν_{max}^{KBr} 3 290, 1 025, 992 1 666, 845; 1 647, 1 411, 897 cm^{-1}. (Found: C 78.1; H 11.1; O 10.5. $C_{20}H_{34}O_2$ requires C 78.4; H 11.2; O 10.4 %).

Isolation of agatholic acid (*7*). Finely divided Manila copal (250 g, m.p. 95—105°) was added to a well stirred suspension of Celite (20 g) in ether (750 ml) and the resulting suspension was stirred for 20 h. After filtration, the solid material was extracted in the same way with a further amount of ether (750 ml). The combined ether solutions were diluted with more ether (1 500 ml) and, after addition of activated charcoal, filtered. The ether solution was extracted twice with alcoholic potassium hydroxide (5 %, 250 ml each time), to which a sufficient amount of water was added to effect separation

into two layers, and then three times with water. The combined aqueous solutions were diluted with water to a total volume of 2 l and acidified with carbon dioxide. The solid material was removed by filtration and the filtrate acidified with ice cold dilute sulphuric acid (10 %) to give crystalline material (10 g), which was removed by filtration and washed repeatedly with water. Recrystallisation from methanol and ethyl acetate gave pure agatholic acid, m.p. 184—186°, $[\alpha]_D$ + 42° (EtOH, *c* 2.0), λ_{max}^{EtOH} 208 mμ (ε 13 000) (Found: C 78.4; H 10.0; O 15.1; equiv. wt. 335. $C_{20}H_{32}O_3$ requires C 75.0; H 10.1; O 15.0; equiv. wt. 320). Agatholic acid methyl ester, m.p. 77—79°, [α] + 44° ($CHCl_3$, *c* 1.0), λ_{max}^{EtOH} 219 mμ (ε 13 000), $\nu_{max}^{CCl_4}$ 1 721 cm^{-1} was obtained in the same way as described for agathic acid dimethyl ester. The mass spectrum of agatholic acid (*7*) includes major peaks at *m/e*: 18 (7), 29 (9), 31 (4), 43 (57), 55 (56), 67 (41), 71 (11), 81 (100), 95 (91), 100 (18), 107 (79), 121 (61), 135 (59), 149 (40), 153 (24; fragmentation A), 163 (24), 175 (20), 189 (27), 203 (16), 245 (46), 261 (17), 275 (7), 289 (27; loss of CH_2OH), 302 (4; loss of H_2O), 305 (4; loss of CH_3), 320 (2; molecular ion).

The figures within brackets give peak intensities as percentages of the strongest peak (81).

Agatholal (*8*). Agathadiol (1.5 g) was dissolved in dry acetone (210 ml) and after addition of manganese dioxide [23] (22 g) the resulting mixture was shaken at room temperature for 10 h. The solid material was filtered off, washed three times with acetone and the combined acetone solutions taken to dryness. The crystalline residue (1.3 g) on recrystallisation from *iso*propyl ether gave agatholal, m.p. 70—72°, $[\alpha]_D$ + 40° ($CHCl_3$, *c* 2.0), λ_{max}^{EtOH} 239 mμ (ε 15 000), $\nu_{max}^{CCl_4}$ 3 655, 3 510, 1 025; 3 090, 1 786, 1 645, 895; 2 770, 1 688; 1 615 cm^{-1}, (Found: C 78.9; H 10.5. $C_{20}H_{32}O_2$ requires C 78.9; H. 10.6) Semicarbazone m.p. 199—201°.

Silver oxide oxidation [8] *of agatholal* (*8*). Agatholal (0.30 g) and finely divided silver nitrate (0.65 g) were dissolved in absolute ethanol (6 ml) and a solution of sodium hydroxide (0.36 g) in aqueous ethanol (1:9, 10 ml) was added dropwise with good stirring. After 24 h at room temperature the mixture was diluted with water, acidified with ice-cold dilute sulphuric acid (5 %) and extracted with ether. The ether solution on drying and evaporation of the solvent gave a crystalline residue (0.30 g) which on sublimation (150°/0.1 mm) and recrystallisation gave pure agatholic acid (*7*), m.p. and mixed m.p. with the natural product 184—186°, $[\alpha]_D$ + 50°. The infrared spectra were superimposable.

Deuterotorulosol (*10*). Torulosal (250 mg) was dissolved in a mixture of dry dioxan (5 ml) and deuterium oxide (2 ml). Sodium (2 g) was added in small pieces to the refluxing solution during 4 h. Deuterium oxide (2 ml) was added to destroy remaining sodium and the reaction mixture was then diluted with water (200 ml) and extracted with ether. After removal of the ether the residue was sublimed at reduced pressure (0.5 mm Hg) and chromatographed on alumina (10 g, activity IV). Elution with a light petroleum (b.p. 35—60°)-ether gradient followed by sublimation gave deuterotorulosol (90 mg), m.p. 110—111°.

The mass spectrum of deuterotorulosol (*10*) includes major peaks at *m/e* = 18 (35), 29 (34), 31 (24), 32 (16; CHDOH), 43 (100), 55 (69), 67 (43), 71 (68; $CH_3C(OH)CH=CH_2$), 81 (76), 95 (57), 107 (40), 121 (34), 133 (20), 147 (17) 154 (13; fragmentation A), 161 (19), 175 (13), 189 (21), 221 (6) 229 (2), 246 (4), 257 (26; loss of CHDOH and H_2O), 274 (4; loss of CH_3 and H_2O), 275 (2; loss of CHDOH), 289 (3; loss of H_2O), 292 (0.8; loss of CH_3), 307 (0.4; molecular ion).

The figures within brackets give peak intensities as percentages of the strongest peak (43).

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