22 %. NMR signals at 60 MHz: 9 H at $\delta=1.51$ (s), and 2 H at $\delta=3.37$ (s), solvent deuterochloroform, internal reference tetramethylsilane. A second fraction, boiling at 104°/4 mm, weighing 8.7 g, was identified as *N-tert*-butylmalonamic acid *tert*-butyl ester, yield 8 %. The latter fraction was obtained as a very viscous oil which solidified when kept at 5°. NMR signals at 60 MHz: 9 H at $\delta=1.37$ (s), 9 H at $\delta=1.48$ (s), 2 H at $\delta=3.15$ (s), and 1 H at $\delta=6.95$ (broad), same solvent and reference as above. The IR spectrum was also in agreement with the proposed structure.

Experiments with less than twice the amount of isobutene as cyanoacetic acid were performed in the same manner. In the one using a mole ratio 1.5:1 for the reactants, the aqueous phase from the work-up was also investigated. After addition of excess aqueous hydrochloric acid, it was extracted three times with 100 ml portions of ether. The combined ethereal extracts were flash evaporated, and the residue dried by azeotropic distillation with benzene. A viscous oil, weighing 8 g, remained. This was only sparingly soluble in water and could not, therefore, consist of unchanged cyanoacetic acid. An NMR spectrum at 60 MHz of the potassium salt (prepared *in situ* in deuterium oxide by the addition of potassium carbonate) displayed, in addition to the water peak, two peaks at the relative positions expected for *tert*-butyl and "acidic" methylene, respectively, and in the ratio of about 12:1. Since the protons of the methylene group may exchange with the solvent, no quantitative significance can be given to this ratio, but one can nevertheless conclude that the aqueous phase contained *N-tert*-butylmalonamic acid.

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20*R*,24 ξ,-Ocotillone, a Triterpenoid from Commercial Tolu Balsam

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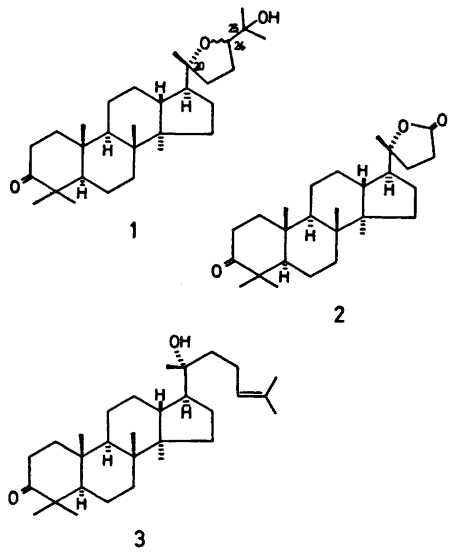
In continuation of an investigation of tolu balsam,[1,2] a commercially available bled resin from *Myroxylon balsamum* (L.) Harms (Leguminosae), the constituents of the hexane soluble neutral fraction have been studied.[3] The non-volatile part of this fraction consists of a complex mixture of triterpenoids of which one, obtained in a pure state by repeated chromatography and subsequent recrystallisations, is found to be a compound previously not encountered in Nature. The present paper gives the evidence on which structure *1* has been assigned to this compound.



The mass spectrum of compound *1* gives valuable structural information. It exhibits important peaks at *m/e* 443 (M − 15), 440 (M − 18), 425 (M − 15 − 18), 399 (M − 59), 381 (M − 59 − 18), 357, 313,

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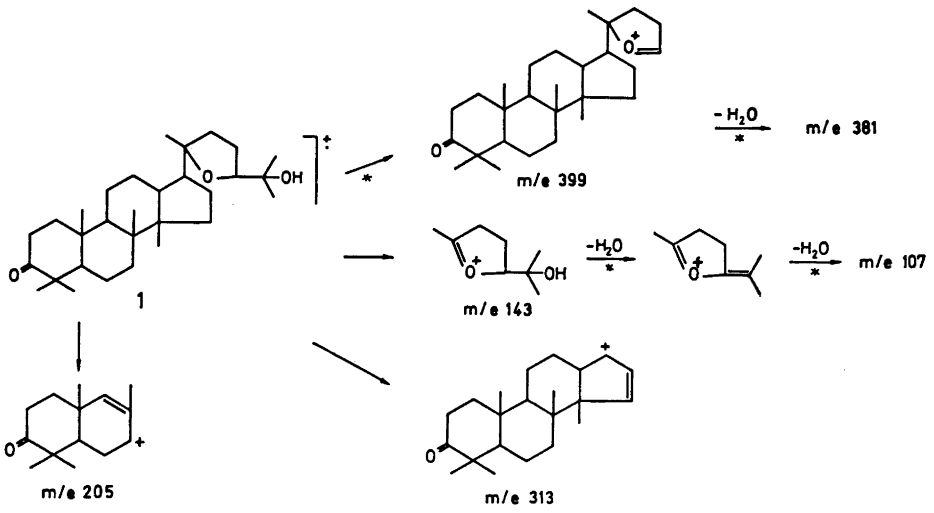

Scheme 1

245, 205, 175, 161, 143, 125, 107, and 59. This characteristic fragmentation pattern, and in particular the favoured formation of the *m/e* 143 fragment ($C_8H_{15}O_2$) together with the presence of the M − 59 peak, suggests that compound *1* is related to ocotillone, a dammarane derivative incorporating an ether-bridged side-chain (*cf.* Scheme 1, which shows proposed structures, based on high-resolution data, for some of the diagnostically important ions).

These findings are corroborated by the NMR spectrum, which displays peaks due to eight tertiary methyl groups at δ 0.88, 0.95, 1.01, 1.04, 1.08, 1.10, 1.14, and 1.19. The first five of these signals have values close to those observed for the methyl groups located in the tetracyclic skeleton in 3-oxo dammarane derivatives.[4] A complex signal at δ 3.68 could be ascribed to the proton attached to the same carbon as the ether oxygen.

Since compound *1* is similar but not identical to the previously isolated isomers, 20*R*- and 20*S*-ocotillone,[5–8] it seemed probable that it only differs from one of these with respect to the configuration at C(24). The absolute configuration at this centre is not established in either of the known isomers. Evidence for this assumption was achieved by oxidation of compound *1* with chromium trioxide in acetic acid, which furnished a trisnorketolactone (*2*) identical with that obtained from 20*R*-hydroxydammarenone (*3*). Final proof was afforded by preparation of the unknown isomer, here designated as 20*R*,24ξ_2-ocotillone, which was accomplished by treatment of 20*R*-hydroxydammarenone (*3*) with 3-chloroperbenzoic acid in ether.[9,10] The resulting mixture of isomers was separated by repeated recrystallisations to give 20*R*,24ξ_2-ocotillone, which proved to be identical with the new naturally occurring compound.

Of the two 20*S*-ocotillol acetates epimeric at C(24), one has been reported to give one 6H singlet and the other two 3H singlets due to the geminal methyl groups at C(25),[9,10] while spectra of previously isolated 20*R*-derivatives show two 3H singlets.[7,11] The observed difference has been used for assignment of the relative configuration at C(24).[11] However, as 20*R*,24ξ_2-ocotillone unexpectedly also gives rise to two 3H singlets, it is evident that identical or different chemical shifts of these peaks cannot be used as a basis for configurational assignments in the 3-oxo series.

Experimental. Melting points were determined on a Kofler micro hot stage and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 257 instrument and NMR spectra on a Varian A-60A spectrometer at

60 MHz. Rotations were measured on a Perkin-Elmer 141 Polarimeter. Low resolution mass spectra were obtained on an LKB 9000 instrument at 70 eV and with an ion-source temperature of 290°. The high resolution measurements were performed on an MS 902 instrument. Liquid chromatography was carried out on silica gel Merck 0.05–0.20 mm (activity I), on $AgNO_3$-impregnated silica and on neutral alumina Schuchardt (activity II) and thin-layer chromatography on silica gel Merck GF.

Isolation. The isolation of the individual triterpenoids from the hexane soluble part of the neutral fraction of an ethanolic solution of commercial tolu balsam (81.9 g per 100 ml solution),[1] required a series of separation steps. Thus, distillation, chromatography on neutral alumina, silica gel and on $AgNO_3$-impregnated silica gel followed by repeated recrystallisations from acetonitrile and isopropyl ether furnished the desired compound, 20*R*,24ξ_2-ocotillone (*1*) m.p. 204–206°; $[\alpha]_D(CHCl_3)+54°$ (*c* 1.0); M−15=443.3518; $C_{29}H_{47}O_3$ requires 443.3525; M−18=440.3650; $C_{30}H_{48}O_2$ requires 440.3654; ν_{max}(KBr): 3575, 3545, 1702, 1450, 1385, 1375, 1328, 1170, 1140, 1082, 1058, 1035, 994, 986, 945, 894 cm^{-1}; $\delta(CDCl_3)$: 0.88, 0.95, 1.01, 1.04, 1.08, 1.10, 1.14, and 1.19 (all 3H singlets), 3.68 (1H,m); *m/e* (%, composition): 443 (2), 440 (0.4), 425 (0.3, $C_{29}H_{45}O_2$), 399 (15,$C_{27}H_{43}O_2$), 381 (2,$C_{27}H_{41}O$), 357 (1,$C_{25}H_{41}O$), 313 (1,$C_{22}H_{33}O$), 245 (1,$C_{17}H_{25}O$), 205 (5,$C_{14}H_{21}O$), 175 (2,$C_{13}H_{19}$), 161 (3,$C_{12}H_{17}$), 143 (100,$C_8H_{15}O_2$), 125 (21), 107 (5), 59 (9,C_3H_7O). 20*R*,24ξ_2-Ocotillone has a slightly higher R_F value on a thin-layer plate developed in isopropyl ether than the previously known isomers, 20*R*- and 20*S*-ocotillone.

*Oxidation of 20*R,*24ξ_2-ocotillone (1).* 20R,24ξ_2-ocotillone (*1*, 7 mg) in acetic acid (2 ml) was treated with chromium trioxide (8 mg) dissolved in acetic acid (0.2 ml) and 3 drops of water, and left overnight at 20°. The reaction mixture was diluted with water and extracted with ether. The ether extract, after washing with saturated aqueous sodium hydrogen carbonate, was concentrated and chromatographed on silica gel (hexane/acetone 1:0 → 1:0.1), to give the trisnorketolactone (*2*), m.p. and mixed m.p. 217–220°. The IR and mass spectra were identical with those of authentic material; $\nu_{max}(CCl_4)$: 1775, 1708 cm^{-1}; *m/e* (%): 414 (24), 399 (4), 396 (4), 381 (2), 371 (2), 329 (6), 328 (6), 316 (12), 315 (14), 287 (10), 205 (51), 195 (20), 99 (100), 81 (68).

*Preparation of 20*R,*24ξ_2-ocotillone (1).* 3-Chloroperbenzoic acid (20 mg) was added to 20*R*-hydroxydammarenone (*3*, 24 mg) in ether (3 ml) and the solution was left at room temperature for 24 h. It was diluted with water and extracted with ether. The ether extract after removal of acids with saturated aqueous sodium hydrogen carbonate gave a mixture of 20*R*-ocotillones epimeric at C(24). Repeated recrystallisation from isopropyl ether furnished 20*R*,24ξ_2-ocotillone (*1*), m.p. 203–205°. The mixed m.p. with the naturally occurring compound was undepressed (203–206°) and the infrared, NMR, and mass spectra were identical.

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