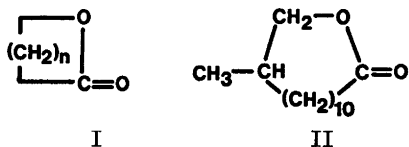


12-Methyl- ω -tridecanolide, A New Macrocyclic Lactone from *Angelica* Root Oil

JYRKI TASKINEN

Research Laboratories of the State Alcohol Monopoly (Alko), Box 350, SF-00101 Helsinki 10, Finland

Three macrocyclic lactones, ω -tridecanolide, ω -pentadecanolide, and ω -heptadecanolide (I, $n = 12, 14,$ and $16,$ respectively), have been found in the root oil of *Angelica archangelica* L.¹⁻³ Recently an unknown compound, which also was supposed to be a macrolide, was reported to be present in this oil, of which it constituted less than 0.1%.³ On the basis of spectral evidence, structure II, 12-methyl- ω -tridecanolide, is now proposed for this lactone.



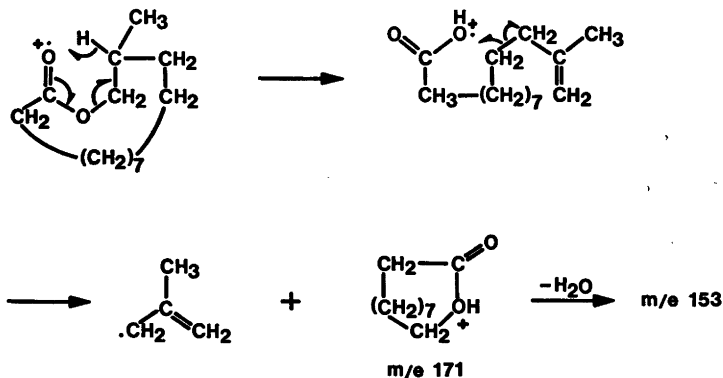
The molecular formula $C_{14}H_{26}O_2$ was evident from the mass, IR and 1H NMR spectra. The mass spectrum was very similar to those of known macrolides, displaying molecular the peak at m/e 226, base peak at m/e 55 and typical $M-18, M-36,$ and $M-60$ fragments.⁴ Some anomalous peaks were present, however, the most abundant of which in the high mass region being at m/e 171 (9%) and 153 (18%). A small peak (2%) for the $M-15$ ion was also observed. The IR spectrum had strong absorption bands at 1735 cm^{-1} ($C=O$) and 1235 cm^{-1} ($C-O$). The spectrum closely resembled those of the other macrolides, except for a band at 1375 cm^{-1} that implied that a methyl group may be present. The NMR signal at δ 0.92

(3 H, d, J 6.8 Hz) confirmed the presence of a methyl on a carbon bearing one hydrogen. Signals centered at δ 3.68 (1 H, doublet of doublets, J 10.7 and 8.3 Hz) and at δ 4.20 (1 H, doublet of doublets, J 10.7 and 3.4 Hz) were evidently due to two mutually coupled protons, both of which are coupled to another proton, and were assigned to a methylene group carrying an oxygen. Decoupling experiments showed that the methylene and the methyl protons were coupled to the same proton. This establishes that the methyl group is on the carbon β to the ether oxygen. A 2 H multiplet centered at δ 2.38 was assigned to the methylene adjacent to carbonyl.

The lactone was hydrolyzed in alcoholic KOH and the hydroxy acid obtained was methylated with diazomethane. The mass spectrum of the methyl ester had its base peak at m/e 55, and a prominent peak characteristic for methyl esters appeared at m/e 74. All peaks of the series m/e 87, 101... up to 199 were present, and no branching in the middle of the chain was apparent from the spectrum. The molecular peak was not observed. In the high mass range the most abundant peak appeared at m/e 228 ($M-30, 78\%$). This peak is probably due to the ion formed by cleavage of the bond between C-12 and C-13 (which carries the hydroxyl group) and rearrangement of one hydrogen atom. Prominent peaks due to ions formed by analogous fragmentation are found in the spectra of some methyl hydroxyoctadecanoates published by Ryhage and Stenhagen.⁵

The corresponding ion ($M-44$) produces the base peak in the spectrum of methyl 17-hydroxyoctadecanoate. Because reference spectra of ω -hydroxyesters were not available, methyl 15-hydroxypentadecanoate was prepared from ω -pentadecanolide. The most prominent peak (28%) in the high mass range in the spectrum of this ester was also produced by the $M-30$ rearrangement ion.

From the NMR data and mass spectrum of the methyl ester it is evident that the com-



Scheme 1.

pound has an ω -lactone ring with only one methyl side chain located on C-12, as in II.

The formation of the ions m/e 171 and 153, analogues of which are not present in the spectrum of unbranched macrolides, can be rationalized as shown in scheme 1. McLafferty rearrangement of the C-12 hydrogen followed by cleavage of the bond β to the newly formed double bond would form a fragment of m/e 171. Loss of water from this ion would produce the m/e 153 ion.

Experimental. Gas chromatography was performed on a Hewlett-Packard 7620 A instrument with 6 mm \times 3 m stainless steel columns packed with 10% FFAP or 5% SE-30 on Chromosorb W AW. IR spectra were recorded on a Perkin-Elmer 521 instrument. Mass spectra were run on a JEOL JMS-D 100 mass spectrometer at the Technical Research Center of Finland. ^1H NMR spectra were determined in CDCl_3 on a JEOL JMM PFT 100 spectrometer in the Department of Organic Chemistry, University of Helsinki.

The isolation of angelica root oil and separation of the fraction containing the oxygenated compounds have been described before.³

12-Methyl- ω -tridecanolide. About 0.2 mg of II was separated gas chromatographically from the oxygenated fraction of angelica root oil.

MS: m/e (%) 226 (M^+ , 5), 211 (2), 208 (14), 198 (4), 196 (5), 193 (3), 190 (3), 171 (9), 160 (8), 165 (8), 153 (18), 152 (11), 139 (9), 124 (14), 111 (25), 98 (41), 97 (36), 84 (34), 83 (42), 69 (67), 56 (61), 55 (100), 41 (96). IR: ν_{max} 2920, 2875, 1735, 1458, 1375, 1345, 1235, 1170, 1145, 1105, 1060, 1007 cm^{-1} . NMR: δ (CDCl_3) 0.92 (3 H, d, J 6.8 Hz), 2.38 (2 H, m), 3.68 (1 H, doublet of doublets, J 10.7 and 8.3 Hz), 4.20 (1 H, doublet of doublets, J 10.7 and 3.4 Hz).

ω -Pentadecanolide was obtained from K&K laboratories.

The lactones were hydrolyzed using 10% alcoholic KOH at room temperature. The hydroxy acids were taken up into pentane and methylated with diazomethane.

1. Kerschbaum, M. *Ber. Deut. Chem. Ges.* 60 (1927) 902.
2. Klouwen, M. H. and ter Heide, R. *Perfum. Essent. Oil Rec.* 56 (1965) 156.
3. Taskinen, J. and Nykänen, L. *Acta Chem. Scand. B* 29 (1975). *In press.*
4. McFadden, W. H., Day, E. A. and Diamond, M. J. *Anal. Chem.* 37 (1965) 89.
5. Ryhage, R. and Stenhagen, E. *Ark. Kemi* 15 (1960) 545.

Received March 25, 1975.

Synthesis of Triallylmethane

GÖRAN LINDGREN and LARS ADOLFSSON

Department of Chemistry, Div. II, Agricultural College, S-750 07 Uppsala 7, Sweden

The aim of this note is to report the preparation of pure triallylmethane (**4a**), which was needed for the synthesis of 2,4,9-trithiaadamantane (**5a**).

In 1963, Shelden¹ treated the Grignard reagent from diallylmethyl chloride (**1a**) with allyl bromide. He obtained about equal amounts of **4a** and an isomer, believed to be 4-allyl-1,7-octadiene (**3a**), but failed to separate the products. In 1968, Reeve and Bianchi² obtained tetraallylmethane (**4b**) and 4-allyl-4-vinyl-1,7-octadiene (**3b**) from triallylmethyl chloride (**1b**) in the same way. They explained the formation of **3b** by the rearrangement shown in Scheme 1.

Following a suggestion by Shelden,¹ we have now prepared **4a** (= **2b**) by hydrolyzing the Grignard reagent from **1b**. 4-Methyl-4-vinyl-1,6-heptadiene (**6b**) was obtained as a by-product but the isomers **4a** and **6b** were cleanly separated by distillation through a spinning band column. Their purity was checked by GLC analysis, and their identity established by ^1H NMR spectroscopy (see Experimental). Thus, the integration of either spectrum showed 7 paraffinic and 9 olefinic protons. The latter belong to three vinyl groups, since the elemental analyses and boiling points confirmed the molecular formula $\text{C}_{10}\text{H}_{16}$. Spin decoupling of the vinyl hydrogens revealed six allylic protons in **4a** and four in **6b**. The coupling of the remaining paraffinic proton in **4a** to all six allylic protons and the absence of further coupling in **6b** exclude alternative structures. As shown in Scheme 1, both **6b** and Shelden's product **3a** are the rearranged hydrocarbons predicted by the mechanism of Reeve and Bianchi.

As might have been expected, the mass spectrum of **4a** showed no molecular peak but was dominated by peaks due to the allyl cation (m/e 41, 100%) and to the loss of an allyl radical (m/e 95, 47%). In the spectrum of **6b**, the former peak (75%) was weaker than the latter (100%). This difference may be due to the fact that the fragmentations of **6b** are doubly allylic. Otherwise, the mass spectra as well as the IR spectra of the two isomers were quite similar.

Experimental. Freshly distilled triallylmethyl chloride (**1b**, 40 g, 0.23 mol) was prepared and converted to the Grignard reagent according to Reeve and Bianchi.² The resulting solution was poured on to a stirred mixture of ether (100 ml), 2 M hydrochloric acid (200 ml) and crushed ice (200 g). The organic layer was separated, washed with water and dried with magnesium sulfate. The ether was removed by rotary evaporation below 20°C and the residue