

CALOZEYLANIC ACID, A NEW BARY ACID FROM THREE  
CALOPHYLLUM SPECIES (GUTTIFERAE)

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**Abstract:** Calozeylanic acid has been isolated from the bark of three Calophyllum species: C.lankaensis (= C.zeylanicum), C.thwaitesii and C.walkerii. Its structure has been established as 2(R),3(R)-2,3-Dimethyl-5-hydroxy-6-(3-methylbutanyl)-6-(3,7-dimethylocta-3,6-dienyl)-7-oxo-8-(2-carboxy-1-phenylethyl)-2,3,6,7-tetrahydrobenzo-4-pyrone.

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Calophyllum lankaensis Kosterm. (= C.zeylanicum Kosterm.), C.thwaitesii Planch & Triana and C.walkerii Wight have been previously investigated in this laboratory and have been shown to biosynthesise prenylated<sup>1,2</sup> and geranyl side chain cyclised<sup>1</sup> xanthenes. The acidic fractions of the bark extractives of these plants eluded structural clarification because of their **complexity** and unusual spectroscopic properties. Nearly 80% of the acid fraction, in each case, was found to be a unique acid designated calozeylanic acid. The present communication deals with its structure determination as (1).

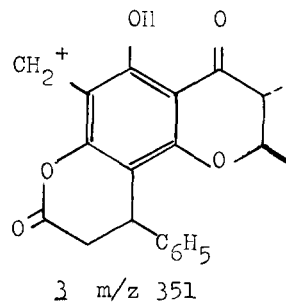
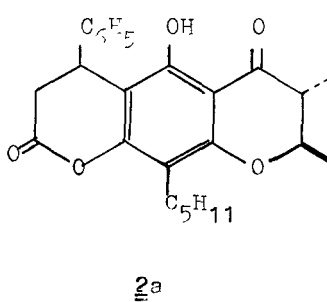
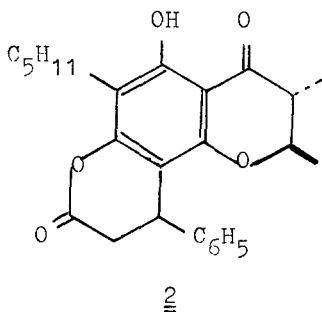
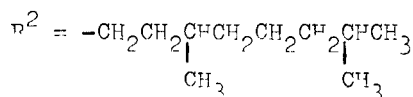
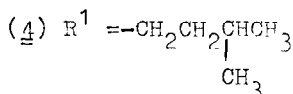
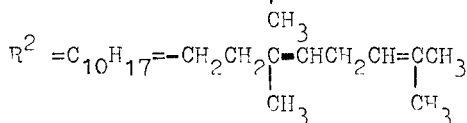
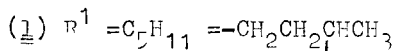
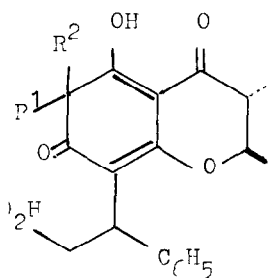
Calozeylanic acid,  $C_{35}H_{46}O_6$ , ( $\alpha$ )<sub>D</sub> + 12.6°(CHCl<sub>3</sub>) could not be crystallised but the product obtained on treatment with *p*-toluenesulphonic acid gave a crystalline lactone (2) m.p. 125-6°, ( $\alpha$ )<sub>D</sub> + 127.7°,  $C_{25}H_{28}O_5$ . This lactone ( $\nu_{max}$  1775 cm<sup>-1</sup>) showed in its <sup>1</sup>H NMR spectrum the presence of five aromatic protons ( $\delta$  7.2), a triplet at  $\delta$  4.5 (J=5Hz) for a low field benzylic proton, a doublet at  $\delta$  2.98 (J=5Hz) for two protons of the type

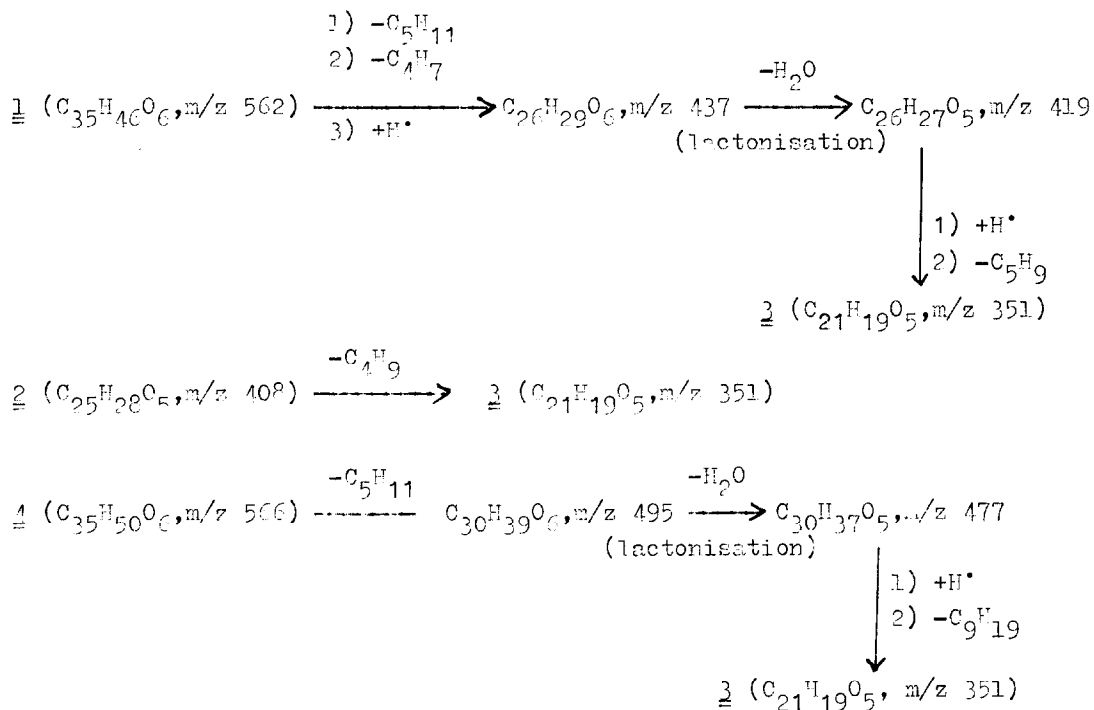
$-\text{CH}_2\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-$  and a chelated OH at  $\delta$  13.9. The lactone readily lost a  $\text{C}_4\text{H}_9$  chain during mass fragmentation and the mass spectrum showed the base peak at  $m/z$  351. High resolution of this ion (2) showed it to have the formula  $\text{C}_{21}\text{H}_{19}\text{O}_5$ . The IR spectrum of the lactone indicated the presence of a monosubstituted phenyl ring ( $760$  and  $698\text{ cm}^{-1}$ ) and a conjugated carbonyl group ( $1665\text{ cm}^{-1}$ ). The evidence for the presence of a 2,2-dimethyl chromanone moiety in the lactone was obtained as follows: The C-2 and C-3 protons appeared as multiplets at  $\delta$  1.7 and 2.1 respectively. The C-2H/C-3H coupling constant was found to be 12Hz indicating a trans-diaxial orientation as in isocaproic acid.<sup>3</sup> The C-3Me protons appeared as a doublet ( $J=6\text{Hz}$ ) centred at  $\delta$  1.10 whereas the C-2Me protons appeared centred at  $\delta$  1.25( $\delta$ ,  $J=6\text{Hz}$ ). From these data the lactone can be represented as either (2) or (2a). The unusually low chemical shifts for the C-2 and C-3 protons of the lactone are due to the orientation of the phenyl substituent, and these chemical shift data were used to rule out the alternative structure (2a) for the lactone. Methylation of the lactone with  $(\text{CH}_3)_2\text{SO}_4$  gave a monomethyl ether. The normal  $^1\text{H}$  NMR signal for -OMe ( $\delta$  3.70) for this ether further confirmed structure (2) for the lactone as against (2a). The nature of the  $\text{C}_5\text{H}_{11}$  side chain in (2) was shown to be isopentanyl, since the molecular ion underwent ready elimination of the  $\text{C}_4\text{H}_9$  chain giving rise to the base peak at  $m/z$  351 and since the  $^1\text{H}$  NMR spectrum of (2) showed the presence of a two-proton triplet for benzylic protons at  $\delta$  2.6( $J=6\text{Hz}$ ) and another two-proton multiplet at  $\delta$  1.7. The signals for Me groups of the side chain appeared along with the chromanone ring protons.

The lactone (2) and tetrahydrocalozeoylanic acid (4) both had their base peaks at  $m/z$  351. Calozeoylanic acid (1) also had an intense fragment ion at  $m/z$  351. The structure of this fragment ion (3) and its formation from the three compounds (Scheme 1) shows that calozeoylanic acid (1) and tetrahydrocalozeoylanic acid (4) both undergo loss of side chains and concomitant lactonisation in the mass spectrometer's probe. The  $^1\text{H}$  NMR spectrum of calozeoylanic acid showed the presence of five aromatic protons ( $\delta$  7-7.4), thirteen allylic protons ( $\delta$  1.4-2.0), two olefinic protons and a one-proton

low field signal ( $\delta$  4.12) which was identified to be due to a benzylic proton. The formation of a tetrahydroderivative on hydrogenation of calozeylanic acid showed the presence of two double bonds in its side chain. Comparison of the  $^1\text{H}$  NMR spectra and molecular formulae of (1) and (2) clearly shows that a geranyl side chain is lost during the formation of (2) from (1) when the latter is treated with *p*-TsOH. On the basis of these data calozeylanic acid has been identified as 2(R),3(R)-2,3-dimethyl-5-hydroxy-6-(3-methylbutanyl)-6-(3,7-dimethylocta-3,6-dienyl)-7-*ortho*-8(2-carboxy-1-phenylethyl)-2,3,6,7-tetrahydrobenzo-4-pyrone (1).

The three *Calophyllum* species under investigation are either montane or mid-montane species. The isolation of the common bark acid from these species is of chemotaxonomic and biogenetic interest. Coastal *Calophyllum* species are currently being investigated for their bark acids.





Scheme-1 : Mass fragmentation of Calozeoylonic acid  
and its derivatives

We thank Professor S.Palacsubramaniam and A.G.J.H.Mostermaans for collecting and identifying the plant materials, Dr. P.Bladon for high resolution mass spectral data and Mrs. S.G.Weerasekera for technical assistance.

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(Received in UK 24 September 1981)