

## A New Sesquiterpene from *Celastrus Angulatus*

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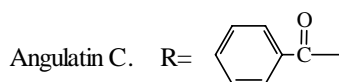
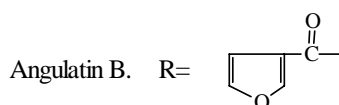
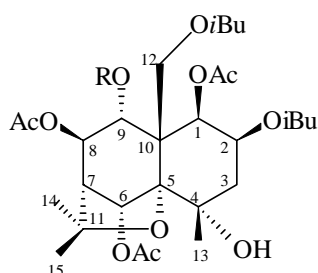
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**Abstract:** One new sesquiterpene polyol ester named angulatin C was isolated from the root bark of *Celastrus angulatus* along with a known compound, angulatin B. Their structures were elucidated on the basis of spectral analysis.

**Keywords:** *Celastrus angulatus*, root bark, sesquiterpene, dihydro- $\beta$ -agarofuran, angulatin C.

In our previous paper<sup>1</sup>, we reported the methodologic studies on authenticating plant species by <sup>1</sup>HNMR finger-prints of the characteristic general extracts of plants. In continuation of our work on this subject, our attention was drawn to the assignments of the signals in the <sup>1</sup>HNMR finger-prints of plants, that was the investigation of the constituents. In the course of our research, a new sesquiterpene polyol ester named angulatin C was isolated from the root bark of *C. angulatus* along with a known compound, angulatin B. In addition to insecticidal activity, angulatin C also showed antibacterial and antiphlogistic activities according to preliminary pharmaceutical tests. Here, we report their structures.

Angulatin C was isolated as an amorphous powder, molecular formula C<sub>36</sub>H<sub>48</sub>O<sub>14</sub> was determined by HRMS. Its IR spectrum showed hydroxyl band at 3506cm<sup>-1</sup> and ester group band at 1743cm<sup>-1</sup>. The 400MHz <sup>1</sup>HNMR spectrum of angulatin C showed signals due to one benzoyl group at  $\delta$  8.01 (2H,m) , 7.46 (2H,m) and 7.60 (1H,m) , two isobutyryl groups at  $\delta$  2.59 and 2.67 (each 1H,sept,J=6.8Hz) , 1.25 and 1.26 (each 6H,d,J=6.8Hz) , and three acetyl groups at  $\delta$  1.64,2.08 and 2.12 (each 3H,s) . The EI/MS exhibited fragment ions attributable to the presence of benzoate (*m/z* 105) , isobutyrate (*m/z* 71) and acetate (*m/z* 43) .



The  $^1\text{H}$ NMR spectrum also showed signals assignable to five methine protons geminal to ester groups at  $\delta$  5.54 (1H, d,  $J=3.6\text{Hz}$ , H-1 $_{\alpha}$ ), 5.29 (1H, dd,  $J=6.8, 3.6\text{Hz}$ , H-2 $_{\alpha}$ ), 6.28 (1H, s, H-6 $_{\beta}$ ), 5.62 (1H, d,  $J=3.6\text{Hz}$ , H-8 $_{\beta}$ ), 5.70 (1H, s, H-9 $_{\alpha}$ ) and one ester-bearing methylene at  $\delta$  4.91 and 4.80 (2H, ABq,  $J=12.8\text{Hz}$ , H $_2$ -12).  $^1\text{H}$ - $^1\text{H}$  COSY spectrum was applied to identify the signals due to H-1, H-2 and H $_2$ -3 ( $\delta$  2.23 and 2.00) as well as H-7 ( $\delta$  2.37) and H-8, and the remaining two signals ( $\delta$  5.70 and 6.28) had to be due to H-9 and H-6, respectively, as the  $^1\text{H}$ NMR chemical shift for H-6 is generally greater than or near to  $\delta$  6.00 when C $_6$ -OH is esterified<sup>2</sup>. The remainders of the  $^1\text{H}$ NMR data of angulatin C are attributable to the protons of three tertiary methyl groups, *i. e.*  $\delta$  1.47, 1.56 and 1.61 (each 3H, s, H $_3$ -13, 14, 15).

In the  $^{13}\text{C}$ NMR spectrum of angulatin C, the relevant signals at  $\delta$  18.68, 18.71, 18.85, 19.01, 33.9, 34.1, 175.2, 176.4[2 $\times$ (CH $_3$ ) $_2$ CHCO], 20.3, 21.0, 21.4, 169.4, 169.6, 169.7 (3 $\times$ AcO), 128.4, 129.4, 130.1, 133.7, 164.5 (m, PhCO), 23.9, 26.3, 29.6 (3 $\times$ CH $_3$ , 13-, 14-, 15-Me), 41.4 (CH $_2$ , 3-C), 53.0 (CH, 7-C), 54.3 (C, 10-C), 65.5 (CH $_2$ , 12-C), 67.9, 70.9, 72.4, 75.3, 76.2 (5 $\times$ CH, 1-, 2-, 6-, 8-, 9-C), 69.9 (C, 4-C), 83.8 (C, 11-C), 91.2 (C, 5-C) ppm were also consistent with the proposed structure. It was decided that angulatin C is a 1,2,4,6,8,9,12-heptasubstituted  $\beta$ -dihydroagarofuran<sup>3,4</sup>. In addition, the molecular composition and IR ( $\nu$ 3506  $\text{cm}^{-1}$ ) suggested the presence of one free hydroxy group. This free hydroxyl was situated at C-4<sup>2,3</sup>.

The axial and equatorial protons of each spin system were distinguished with the aid of their coupling constants. In addition, the very sharp upfield singlet at  $\delta$  1.64 (3H) for one acetate methyl suggested the possible location of this acetate ester and the benzoate ester at C-1 and C-9 (or C-9 and C-1), respectively<sup>3</sup>. The intense mass spectral ion at  $m/z$  202 confirmed that the benzoate ester is situated at C-9, the acetate ester is thus at C-1<sup>3</sup>. The mass spectrum of angulatin C also exhibited three peaks due to the sequential loss of three acetic acid units:  $m/z$  556 [616-HOAc] $^+$  (3), 496[556-HOAc] $^+$  (3) and 436 [496-HOAc] $^+$  (4). This indicated that no acetate ester is situated at C-12, but rather an isobutanoate ester. The relatively intense McLafferty rearrangement peak at  $m/z$  616 [M-C $_3$ H $_7$ CO $_2$ H] $^+$  (6) in the mass spectrum suggested the location of isobutanoate ester at C-2<sup>4</sup>. The same conclusion could be acquired from the HMBC spectrum of angulatin C. Thus, the structure of angulatin C is 1 $\beta$ , 6 $\alpha$ , 8 $\beta$ -triacetoxy-2 $\beta$ , 12-diisobutyroloxy-9 $\alpha$ -benzyloxy-4 $\alpha$ -hydroxy- $\beta$ -dihydroagarofuran.

The structure of angulatin B was elucidated in the same way as in angulatin C. It was previously reported as a constituent of *C. gemmatus*<sup>4</sup>.

### Acknowledgments

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### References

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