CHEMICAL CONSTITUENTS AND BIOLOGICAL ACTIVITY OF CELASTRACEAE PLANTS

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I. INTRODUCTION

Dihydroagarofuran sesquiterpenoids are the main chemical constituents of Celastraceae plants[1]. Since the Celastraceae plants were used as agricultural insecticides[2 — 5], we are quite interested in the investigation on the insecticidal activity of this kind of compound. Our previous note reported that three sesquiterpenoids (**1** — **3**) were isolated from *Celastrus gemmatus* Loes., and their structures were determined on the basis of IR, NMR and mass spectrometry, and X-ray diffraction[6,7]. Recently, in order to further investigate the biological activity, two new sesquiterpenoids (**4**, **5**) have been isolated from *Celastrus rosthornianus* Loes. This note reports the structures of **4** and **5**, and the insect antifeedant and insecticidal activities of compounds **1** — **5** against the insects of *Pieris rapae* which usually exist on crops.

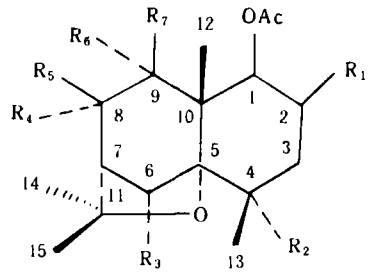
II. ISOLATION AND IDENTIFICATION OF CHEMICAL CONSTITUENTS

The air-dried and pulverized root bark of *C. rosthornianus* was extracted with acetone at room temperature for two days. The removal of the solvent under reduced pressure afforded a sticky residue, which was later chromatographed on an eluent neutral Al_2O_3 column with $CHCl_3$ silica gel preparative plants with acetone-benzene (1 : 4) and reverse phase preparative plates with MeOH — H_2O in turn to yield compounds **4**(0.02%) and **5**(0.05%).

Compound **4**: ^{1}HNMR (400 MHz, TMS, $CDCl_3$, δ/ppm): 5.62 (1H, d, J = 3.5 Hz, H — 1), 5.89 (1H, dd, J = 3.5, 6.8 Hz, H — 2), 2.20 — 2.31 (2H, m, H — 3), 5.12 (1H, d, J = 5.4 Hz, H — 6), 2.63 (1H, d, J = 3Hz, H — 7), 5.59 (1H, d, J = 3Hz, H — 8), 5.19 (1H, s, H — 9), 1.88, 1.93, 1.71 and 1.68 (4 × 3H, 4 × s, H — 12, 13, 14 and 15), 1.57(3H, s, OAc), 7.48 — 8.03 (15H, m, 3 × OBz). ^{13}CNMR (400 MHz, TMS, $CDCl_3$, δ/ppm):

70.1(C — 1), 69.0(C — 2), 40.9 (C — 3), 72.2(C — 4), 91.8 (C — 5), 75.0(C — 6), 54.5(C — 7), 76.0(C — 8), 76.4(C — 9), 49.5(C — 10), 84.2(C — 11), 21.7(C — 12), 25.5(C — 13), 26.2(C — 14), 30.5(C — 15). The ^{1}HNMR spectrum of **4** indicates that this compound contains one acetate ester and three benzoate esters. The ^{13}CNMR spectrum indicates that the parent is a 1, 2, 4, 6, 8, 9-hexasubstituted-β-dihydroagarofuran[8]. Therefore, in addition to the four ester groups mentioned above, **4** should contain two other substituents. The IR absorptions at ν3468 and 3423 cm^{-1} indicate that these two substituents are free hydroxy groups. The ^{1}H – ^{13}C long-range COSY (COLOC) spectrum indicates that three benzoate esters are situated at C – 2, C – 8 and C – 9, respectively. Furthermore, the upfield chemical shift (δ1.57) for the acetate ester indicates that this group is situated at C – 1[2]. Thus the two free hydroxy groups are situated at C – 4 and C – 6, respectively. Based on the evidence above, the structure of **4** has been elucidated.

Compound **5**: ^{1}HNMR (400 MHz, TMS, $CDCl_3$, δ/ppm): 5.50 (1H, d, J = 4Hz, H – 1), 5.65 (1H, dd, J = 4, 7Hz, H – 2), 2.20 – 2.40 (2H, m, H – 3), 5.07 (1H, d, J = 5.4 Hz, H – 6), 2.60 (1H, d, J = 3.2Hz, H – 7), 5.56(1H, d, J = 3.2Hz, H – 8), 5.16 (1H, s, H – 9), 1.86, 1.77, 1.68 and 1.66(4 × 3H, 4 × s, H – 12, 13, 14 and 15), 1.57 (3H, s, OAc), 7.44 – 8.09 (10H, m, 2 × OBz), 0.91(3H, t, J = 7Hz), 1.16 (3H, d, J = 7Hz) and 1.20 — 2.40 (3H, m) (α-methylbutanoyloxy). ^{13}CNMR (400 MHz, TMS, $CDCl_3$, δ/ppm): 70.2 (C – 1), 67.7 (C – 2), 41.3(C – 3), 72.3(C – 4), 92.1(C – 5), 75.1(C – 6), 54.7(C – 7), 76.3(C – 8), 76.7(C – 9), 49.7(C – 10), 84.2(C – 11), 21.8 (C – 12), 25.4(C – 13), 26.3(C – 14), 30.6(C – 15). The structure of **5** has been elucidated by means of the same method used in **4**.



1 R1 = R2 = R3 = R4 = R5 = R7 = H, R6 = PhCH = $CHCO_2$:

2 R1 = OAc, R2 = R3 = R4 = R5 = R7 = H, R6 = PhCH(O)$CHCO_2$

3 R1 = R2 = R5 = R6 = H, R3 = R4 = OAc, R7 = OBz

4 R1 = R5 = R6 = OBz, R2 = R3 = OH, R4 = R7 = H

5 R1 = $CH_3CH_2(CH_3)CHCO_2$, R2 = R3 = OH, R5 = R6 = OBz, R4 = R7 = H

III. Experiment for Biological Activity[9]

1. *Leaf Painting*

The test sample was made into acetone solution (2000 ppm). Each wild cabbage leaf was painted with 10μl sample solution, corresponding to 20 μg for each. After the leaves were dried in air the larvae of *P. rapae* were fed with them, and weighed after 24 and 72 h respectively. The control group was tested using pure acetone in the same way, and the test results are listed in Table 1. From Table 1, it can be found that compound **1** shows relatively high insecticidal and insect antifeedant activities, and its death rate and antifeedant rate are 40% and 41.5%, respectively.

2. *Leaf Maceration*

The test sample was made into acetone solution (200 ppm). The wild cabbage leaves

were macerated in this solution for a while. After the leaves were dried in air the larvae of *P. rapae* were fed with them and weighed after 48 h. The control group was tested using pure acetone in the same way, and the results are listed in Table 2. From Table 2, it can be found that compound **3** shows the relatively high insect antifeedant activity, the anifeedant rate is 63.4%, while compound **2** shows the relatively high insecticidal activity, and the corrected death rate is 44%.

Table 1

Biological Activities of Compounds Against Insects of *Pieris rapae* (Leaf Painting)

Compound	Concentration (ppm)	Eaten Leaf Area (mm^2/ head)	Weight Enhancement (mg/ head)		Antifeedant Rate (%)	Death Rate (%)
			24h	72h		
1	2000	351	44.5	56.6	41.5	40
2	2000	559	50.0	79.6	6.7	10
3	2000	650	50.3	56.6	0	20
4	2000	487	31.4	23.0	18.7	10
5	2000	542	40.0	65.2	9.5	20
Control		600	81.2	65.8	0	0

Table 2

Biological Activities of Compounds Against Insects of *P.rapae* (Leaf Maceration)

Compound	Concentration (ppm)	Eaten Leaf Area (mm^2/ head)	Antifeedant Rate (%)	Weight Enhancement (mg/ head)	Corrected Death Rate (%)
1	200	1008	31	31.8	11
2	200	1214	17	41.7	44
3	200	547	63.4	17.3	22
4	200	1291	11	55.8	0
5	200	1145	21.2	61.9	22
Control		1452		44.6	0

Table 3

Biological Activities of Compounds Against Insects of *P. rapae* (Leaf Maceration)

Compound	Concentration (ppm)	Eaten Leaf Area (mm^2/ head)	Antifeedant Rate (%)	Death Rate (%)	Corrected Death Rate (%)
1	500	1164	21	12.5	0
2	500	1308	11	50	43
3	500	868	41	25	14
4	500	787	47	0	0
5	500	824	44	12.5	0
Control		1464		12.5	0

3. *Leaf Maceration*

The test sample was made into acetone solution(500 ppm). The wild cabbage leaves were macerated in this solution for a while. After the leaves were dried in air, they were used to feed the larvae of *P. rapae* which had been weighed and denied food for 3 h. The control

group was tested using pure acetone in the same way, and the results are listed in Table 3. From Table 3, it can be found that compounds **3**, **4** and **5** show the relatively high insect antifeedant activities, their antifeedant rates are 41%, 47% and 44%, respectively, while compound **2** shows the relatively high insecticidal activity, its death rate and corrected death rate are 50% and 43% respectivety.

From these three experiments mentioned above, it can be found that the biological activities of these compounds against the insects of *P. rapae* are related to the experimental methods. To sum up, these three constituents isolated from *C. gemmatus* exhibit moderately not only the insect antifeedant activities, but also the insecticidal activities, but those isolated from *C. rosthornianus* do not exhibit obvious insecticidal activities, but only the insect antifeedant activities are shown in one of the three experiments.

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