# Three New Glyceroglycolipids from *Serratula strangulata*

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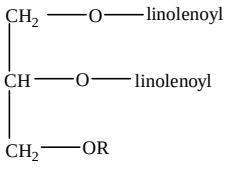
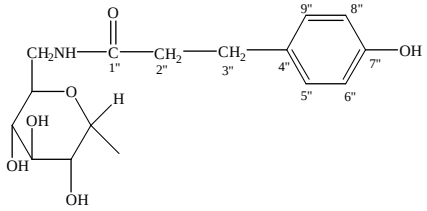
**Abstract:** Three new glyceroglycolipids, strangulatoside A **1**, B **2** and C **3,** were isolated from the stems of *serratula strangulata* (Compositae). Their structures were elucidated on the basis of spectral data, especially 2DNMR methods and chemical conversion.

**Keywords:** Strangulatoside A, B, C, *serratula strangulata*, glyceroglycolipids, Compositae.

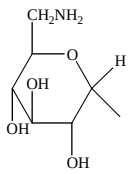
*Serratula strangulata* (Compositae) is a perennial herb distributed in Hebei, Shanxi, Ningxia and Gansu province of China. Its rhizome has been used as a traditional chinese medicine since ancient times[1]. Three new glyceroglycolipids, strangulatoside A, B, C, have been isolated from the alcoholic extract of this herb. Their structures were elucidated on the basis of spectral data, especially 2DNMR methods and chemical conversion.



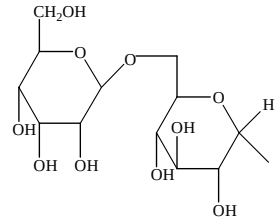

**2.** R =




**1.** R =




**3.** R =



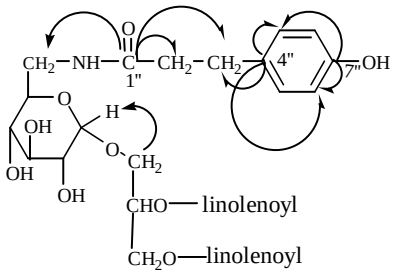

Compound **1** was isolated as colorless gum. $[\alpha]_D^{24}$: +25.5 (C, 3.01, MeOH). FAB-MS which gave quasi-molecular ion peak at *m/z*:796 $(M+Na)^+$, 780 $(M+Li)^+$, as well as its elemental analysis (found: C 69.85%, H 9.70%, N 1.80%; required: C 69.86%, H 9.70%, N 1.81%) indicated that the molecular formula should be $C_{45}H_{75}NO_9$. Its IR spectra showed strong absorptions for hydroxyl and ester groups (3464 $cm^{-1}$, 1729 $cm^{-1}$),

while the $^1$HNMR spectra exhibited two terminal methyl signals ( $\delta$ 0.82, 0.90, 3H each, both t), a broad methylene signal at 1.23 ppm, and the signal ( $\delta$ 2.26, 2.30, 4H, m) due to two methylene protons linked to a carbonyl function. These were consistent with the proton signals of two linolenic acid[2]. Additionally, $^1$HNMR also showed glucose proton signals. The configuration at C-1' of the sugar was determined to be $\alpha$ by the coupling constant of the anomeric proton (J=3.5 Hz). The $^{13}$CNMR and DEPT spectra of **1** confirmed the presence of linolenic acid[3] and an α-aminoglucose moiety (**Table 1**). Simultaneously, they also revealed three carbon signals connected to oxygen atom: $\delta_C$ 62.62 ($CH_2$), 69.73 (CH) and 64.63 ($CH_2$), which ascribed to the presence of a glyceryl moiety. The sites of attachment of the two linolenic acids and aminoglucose moiety of **1** were determined to be at C-1, C-2, C-3 respectively, by means of the HMBC, $^1$H$^1$HCOSY and HMQC spectra.

Because the upfield shift of C-6' in the aminoglucose observed in $^1$HNMR and $^{13}$CNMR, the amine group should be attached to C-6'. Thus, the structure of **1** was assigned as strangulatoside A.

Compound **2** was isolated as colorless gum. $[\alpha]_D^{24}$: +25.8 (C, 2.70, MeOH). FABMS showed $[M+Na]^+$ at *m/z* 944 and $[M+Li]^+$ at 928. Its $^1$H, $^{13}$C and DEPT spectra were similar to those of **1**. In the $^1$H, $^{13}$CNMR of **2**, the extra signals at $\delta_H$ 7.02 (dd, J=7.2, 2.1Hz), 6.69 (dd, J=7.2, 2.1Hz) and $\delta_C$ 40.12 ($CH_2$), 32.22 ($CH_2$), 172.48 (ester C=O) revealed the presence of a *p*-substituted benzene ring and the partial structure -$CH_2$-$CH_2$- and carbonyl group. $^1$H$^1$HCOSY and HMQC spectra confirmed above assignments. According to the results of HMBC spectra: C-1"/ H-6', H-2", H-3"; C-4" / H-3", H-5" (9"); C-7" / H-6" (8") (**Figure 1**), the structure of **2** was deduced as strangulatoside B.

**Figure 1**. The key correlations of **2** in HMBC (C → H)




Compound **3** was obtained as colorless gum. $[\alpha]_D^{24}$: +25.3 ( C, 6 .05, MeOH). The IR spectra of **3** showed absorption bands due to hydroxyl and ester carbonyl at 3460, 1729 $cm^{-1}$. The molecular formula $C_{51}H_{84}O_{15}$ was established on the basis of the strong quasi-molecular ion peak at *m/z* 959 $[M+Na]^+$ and 943 $[M+Li]^+$ in the FABMS, together with the support of combined spectroscopic methods ($^1$HNMR, $^{13}$CNMR and DEPT).

The $^{1}H$ and $^{13}C$NMR spectra of **3** showed that **3** had the same skeleton and type as **1**, **2**. Detailed analysis of the remaining signals in the $^{1}H$ and $^{13}C$NMR spectra of **3** suggested that **3** possessed an allose moiety attached to the inner glucose unit. On acid hydrolysis with 2 mol/l HCl, **3** gave glucose and allose, and on acid hydrolysis with 0.5 mol/l HCl, **3** afforded only allose (identified by TLC). Above deduction was confirmed. The $\beta$-configuration of the glucosidic bond between the glucose and allose residue was determined on the basis of anomeric carbon signal at 103.2 ppm. The observation of the downfield shift of the C-6' carbon confirmed $\alpha$1-6 linkage of the two glucide units[4]. Thus, the structure of **3** was assigned as strangulatoside C, which was further supported by HMBC and HMQC analysis.

Compound **1**, **2**, **3** exhibited antibacterial activity against *B. subtilis, E. coli* and *S. aureus*. The results were compared with chloramphenicol and are summarized in **Table 2**.

**Table 1** $^{13}C$ NMR data for **1**, **2** and **3** (100.62MHz, DMSO-$d_6$, TMS)*

| Carbon | **1** | DEPT | **2** | DEPT | **3** | DEPT |
|---|---|---|---|---|---|---|
| Sn-1 | 62.62 | $CH_2$ | 62.62 | $CH_2$ | 62.46 | $CH_2$ |
| Sn-2 | 69.73 | CH | 69.71 | CH | 69.65 | CH |
| Sn-3 | 64.63 | $CH_2$ | 64.14 | $CH_2$ | 66.42 | $CH_2$ |
| | $\alpha$-aminoglu | | $\alpha$-aminoglu | | $\alpha$-glu | |
| 1′ | 98.29 | CH | 98.31 | CH | 99.59 | CH |
| 2′ | 71.56 | CH | 71.61 | CH | 71.29 | CH |
| 3′ | 72.86 | CH | 72.92 | CH | 72.94 | CH |
| 4′ | 74.13 | CH | 74.16 | CH | 69.76 | CH |
| 5′ | 68.53 | CH | 68.53 | CH | 71.47 | CH |
| 6′ | 54.38 | $CH_2$ | 54.88 | $CH_2$ | 66.67 | $CH_2$ |
| | | | amido moiety | | $\beta$-allo | |
| 1″ | | | 172.48 | C | 103.20 | CH |
| 2″ | | | 40.38 | $CH_2$ | 70.68 | CH |
| 3″ | | | 32.21 | $CH_2$ | 70.35 | CH |
| 4″ | | | 129.54 | C | 66.35 | CH |
| 5″, 9″ | | | 127.68 | CH | 73.18 | CH |
| 6″, 8″ | | | 115.34 | CH | 60.63 | $CH_2$ |
| 7″ | | | 156.17 | C | | |

*Assignment from $^{1}H^{1}H$ COSY, HMQC and HMBC.

**Table 2** Antibacterial activity of compound **1**, **2**, **3**[a]

| | *B.subtilis* | *E.coli* | *S.aureus* |
|---|---|---|---|
| Compound **1** | + | + + + | + |
| Compound **2** | + + | + + + | + |
| Compound **3** | + + | + + | + |
| Chloramphenicol | + + + | + + + | + + + |

[a] Antimicrobial activity is defined as follows: +++ = the diameter is equal to 16-20mm; ++ = 13-15mm; + = 10-12mm.

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