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# GERMACRANOLIDES FROM *LYCHNOPHORA* SPECIES*

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**Key Word Index**—*Lychnophora sellowii*; *L. bahiensis*; *L. crispa*; *L. blanchetii*; Compositae; Vernonieae; sesquiterpene lactones; heliangolides; germacranolides; bisabolene derivative.

**Abstract**—The investigation of three further *Lychnophora* species and the re-investigation of one species afforded, in addition to known compounds, seven new sesquiterpene lactones all being closely related to those isolated before from the subtribe Lychnophorinae. Furthermore, a new bisabolene diketone was present in one species. The structures were elucidated by spectroscopic methods. The chemotaxonomic situation of the genus is briefly discussed.

## INTRODUCTION

The genus *Lychnophora* is placed in the subtribe Lychnophorinae [1]. So far phytochemical investigations have shown that furanoheliangolides are characteristic for this genus and perhaps also for the subtribe [2]. However, oxidized caryophyllene and humulene derivatives are also frequently found [2]. We have now investigated three further species and re-investigated one other. Again furanoheliangolides and closely related sesquiterpene lactones were isolated, seven of which have not been reported previously.

## RESULTS AND DISCUSSION

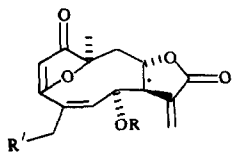
The aerial parts of *L. sellowii* Sch. Bip. afforded *ent*-kaurene, lupeol and its acetate, the pentayne **17**, eremanthin (**10**) [3], the heliangolides **1** [4] and **2** [5], as well as the isomeric carbinols **5** and **6**. The structures **5** and **6** followed from the $^1$H NMR spectra (Table 1). The spectrum of **6** was similar to that of the corresponding methylacrylate, isolated previously from a *Vanillosmopsis* species [6], while that of **5** was similar to that of an acetate formed by a re-arrangement on acetylation of goyazensolide [7] and to some furanoheliangolides [8]. Spin decoupling allowed the assignment of all signals. As usual in heliangolides $J_{7,8}$ was small in both isomers. The presence of 8, 12-lactones was deduced from the chemical shifts and the typical splitting of the H-8 signals, while the nature of the ester group followed from the characteristic angelate signals. Furthermore, three bisabolene derivatives were isolated: the known ketone **14** [9], the hydroxy diketone **16** [10] and the diketone **15**, the structure of which clearly followed from the $^1$H NMR spectral data (Table 2). While the signals of the ring protons were identical with those of **14** and **16**, those of the side chain were changed in the expected manner. Two double doublets at $\delta$ 2.42 and 2.34 were obviously the H-8 signals. Irradiation at $\delta$ 2.78 changed these signals to two doublets, while the methyl doublet at $\delta$ 0.87 collapsed to a singlet, indicating that the H-7 signal was saturated. The rela-

Table 1. $^1$H NMR spectral data of compounds **5**, **6**, **8** and **9** (400 MHz, $CDCl_3$, TMS as int. standard)

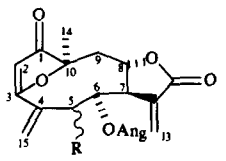
| | **5** | **6** | **8** | **9** |
|---|---|---|---|---|
| H-2 | 5.96 *s* | 5.95 *s* | 5.74 *s* | 5.70 *s* |
| H-5 | 4.88 *dd* | 4.67 *d(br)* | 6.32 *dq* | 6.34 *dq* |
| H-6 | 4.83 *d* | 4.64 *dd* | 5.04 *ddq* | 5.02 *ddq* |
| H-7 | 4.19 *dddd* | 3.65 *dddd* | 2.89 *dd* | 2.88 *dd* |
| H-8 | 4.34 *ddd* | 4.36 *ddd* | 4.18 *ddd* | 4.17 *ddd* |
| H-9$\alpha$ | 2.55 *dd* | 2.49 *dd* | 2.10 *dd* | 2.10 *dd* |
| H-9$\beta$ | 2.36 *dd* | 2.37 *de* | 2.47 *dd* | 2.43 *dd* |
| H-13 | 6.23 *d* | 6.28 *d* | 1.26 *s* | 1.24 *s* |
| H-13′ | 5.49 *d* | 5.54 *d* | | |
| H-14 | 1.57 *s* | 1.53 *s* | 1.50 *s* | 1.49 *s* |
| H-15 | 5.91 *s* | 6.24 *d(br)* | 4.39 *d* | 4.79 *ddd* |
| H-15′ | 5.87 *s* | 6.00 *d(br)* | | 4.76 *ddd* |
| H-3′ | — | — | 5.62 *qq* | 5.61 *qq* |
| H-4′ | — | — | 1.79 *dq* | 1.77 *dq* |
| H-5′ | — | — | 1.83 *dq* | 1.82 *dq* |
| OCOR | 6.09 *qq* | 6.09 *qq* | — | — |
| | 1.89 *dq* | 1.87 *dq* | — | — |
| | 1.79 *dq* | 1.78 *dq* | — | — |
| OAc | — | — | — | 2.11 *s* |

*J*(Hz): Compound **5**: 5,6 = 5,15 < 0.5; 5,OH = 5.5; 6,7 = 6; 7,8 = 1.5; 7,13 = 3.5; 7,13′ = 3; 8,9$\alpha$ = 12; 8,9$\alpha$ = 1.5; 9$\alpha$,9$\beta$ = 14; compound **6**: 5,6 = 9; 5,15 = 1.5; 6,7 = 5; 7,8 = 2; 7,13 = 3.5; 7,13′ = 3; 8,9$\alpha$ = 12; 8,9$\beta$ = 2; 9$\alpha$,9$\beta$ = 14; compound **8** and **9**: 5,6 = 2.5; 6,7 = 7.5; 7,8 = 4; 8,9$\alpha$ = 12; 8,9$\alpha$ = 2.5; 9$\alpha$,9$\beta$ = 14; 3′,4′ = 7; 3′,4′ = 4′,5′ = 1.5 (*compound* **8**; 5.15 = 6,15 = 1.5; 15,15′ = 12; compound **7**: 15,OH = 4).

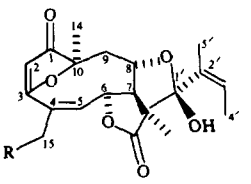
*Part 397 in the series "Naturally Occurring Terpene Derivatives". For Part 396 see Bohlmann, F., Singh, P. and Jakupovic, J. (1982) *Phytochemistry* **21**, 939.



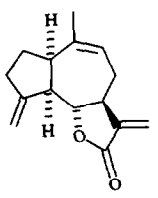
| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| R | Ang | Ang | Meacr | Tigl |
| R′ | H | OH | H | H |



**5** R = α-OH
**6** R = β-OH



**7** R = H
**8** R = OH
**9** R = OAc



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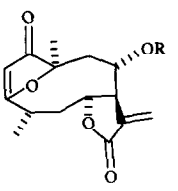
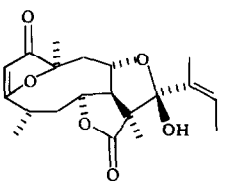


**11** R = Ang
**12** R = Tigl



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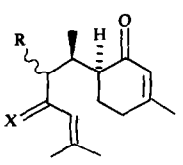
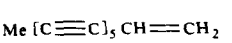
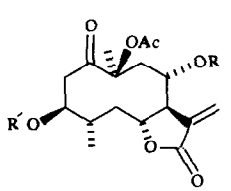


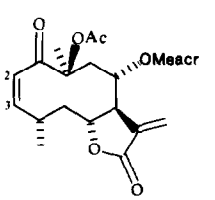
| | 14 | 15 | 16 |
|---|---|---|---|
| X | $H_2$ | O | O |
| R | H | H | OH |



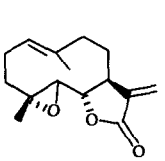
**17**



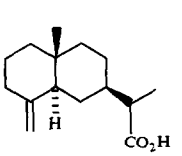
| | 18 | 19 | 20 |
|---|---|---|---|
| R | Meacr | Ang | Meacr |
| R′ | Me | H | H |



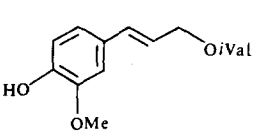
**21** 2,3 trans
**22** 2,3 cis



**23**



**24**



**25**

Table 2. $^1$H NMR spectral data compound **15** (400 MHz, $CDCl_3$, TMS as int. standard)

| | | | |
|---|---|---|---|
| H-2 | 5.83 *q* | H-10 | 6.11 *qq* |
| H-4 | 2.31 *m* | H-12 | 2.12 *d* |
| H-5 | 1.97 *m* + 1.83 *m* | H-13 | 1.88 *d* |
| H-6 | 2.15 *ddd* | H-14 | 0.87 *d* |
| H-7 | 2.78 *dddq* | H-15 | 1.93 *d* |
| H-8 | 2.42 *dd* | | |
| H-8' | 2.34 *dd* | | |

*J*(Hz): 2,4 = 1; 6,7 = 7,14 ~ 7; 7,8 = 6.5; 7,8' = 8; 8,8' = 15; 10,12 = 10,13 = 1; 5,6 = 4.5; 5',6 = 11; 6,7 = 4.5.

tive stereochemistry at C-6 and C-7 followed from the observed coupling. The absolute configuration was not determined.

The aerial parts of *L. bahienis* Mattf. afforded squalene, lupenone, lupeol, the pentayne **17**, the heliangolides **1**, **2** and **3**[7] as well as the eremantholide derivatives **7**[11], **8** and **9**. The structures of **8** and **9** followed from the $^1$H NMR spectra, which, of course, were similar to that of **7** (Table 1). All the signals were assigned by spin decoupling. In the spectra of **8** and **9** the signal of the C-4 methyl group was replaced by the signals of a $CH_2OH$ and $CH_2OAc$ group respectively. While **8** showed a broadened doublet which collapsed to a singlet after deuterium exchange, **9** displayed a pair of doublet triplets due to allylic and homoallylic couplings with H-5 and H-6. As usual, the oxygen function at C-15 caused a downfield shift of the H-5 signal. The roots afforded lupeol, its acetate, lupenone, dehydrocostus lactone, **1**, **3**, **10** and **17**.

The aerial parts of *L. crispa* Mattf. also contained several furanoheliangolides. In addition to **1** and **4**[12], the 4,5-dihydro compounds **11**[6] and **12**[8, 12] as well as **7** and **8** together with **13**[12] were isolated. Furthermore, lupeol and its acetate were again present. The roots afforded **17**, also isolated from the aerial parts, lupeol and its acetate as well as small amounts of **10**.

A re-investigation of the roots of *L. blanchetii* (Sch. Bip.) H. Robins. gave, in addition to compounds isolated previously [13], costic acid (**24**) and the isoeugenol derivative **25**, while the aerial parts afforded the sesquiterpene parthenolide (**23**)[14] and the lactones **18**–**21**. **19** had been previously isolated from *Eremanthus glomerulatus*[14]. Consequently, the $^1$H NMR spectral data (Table 3) of **20** were nearly identical with those of **19**, and were slightly different from those of **18** (Table 3). The $^1$H NMR spectrum of **21** (Table 3) clearly showed the presence of a *trans*-disubstituted double bond, which was in conjugation with the keto group. Heating of **20** with acetic anhydride afforded **21**, its spectral data were completely identical with those of the natural compound. Therefore, the stereochemistry of **20** and **21** were identical at C-4–C-10. In addition to **21**, small amounts of the 2,3-*cis* isomer **22** was also obtained from **20** by heating with acetic anhydride, as could be visualized from the $^1$H NMR spectral data (Table 3). The correspond-

Table 3. $^1$H NMR spectral data of compounds **18** and **20**–**22** (400 MHz, $CDCl_3$, TMS as int. standard)

| | **18** | **20** | **21** | **22** |
|---|---|---|---|---|
| H-2 | 3.19 *dd*(*br*) | 3.15 *dd* | 6.53 *dd* | 6.55 *d* |
| H-2' | 2.74 *dd* | 2.89 *dd* | | |
| H-3 | 3.68 *ddd* | 4.23 *ddd*(*br*) | 6.72 *dd* | 5.94 *dd* |
| H-4 | 2.13 *m* | 2.10 *m* | 2.95 | 3.49 *ddd* |
| H-5 | 2.05 *m** | | 2.22 *ddd* | 1.79 *ddd* |
| H-5' | 1.47 *ddd* | 1.51 *ddd* | 1.97 *ddd* | 1.48 *ddd* |
| H-6 | 4.46 *ddd* | 4.48 *ddd* | 4.91 *ddd* | 4.30 *dd*(*br*) |
| H-7 | 2.95 *dddd* | 2.98 *dddd* | 3.09 *dddd* | 3.13 *d*(*br*) |
| H-8 | 4.92*ddd* | 4.94*ddd* | 5.24*d*(*br*) | 4.80*ddd* |
| H-9 | 2.63 *dd* | 2.64 *dd* | 2.47 *dd* | 2.73 *dd* |
| H-9' | 2.17 *d*(*br*) | 2.19 *d*(*br*) | 2.04 *d*(*br*) | 2.12 *d*(*br*) |
| H-13 | 6.31 *d* | 6.33 *d* | 6.39 *d* | 6.32 *d* |
| H-13' | 5.69 *d* | 5.71 *d* | 5.74 *d* | 5.74 *d* |
| H-14 | 1.88 *s* | 1.88 *s* | 1.85 *s* | 1.85 *s* |
| H-15 | 1.10 *d* | 1.13 *d* | 1.33 *d* | 1.11 *d* |
| OMe | 3.39 *s* | — | — | — |
| OCOR | 6.11 *s*(*br*) | 6.11 *s*(*br*) | 6.02 *s*(*br*) | 6.11 *s*(*br*) |
| | 5.63 *dq* | 5.64 *dq* | 5.59 *dq* | 5.61 *dq* |
| | 1.92 *s*(*br*) | 1.93 *s*(*br*) | 1.86 *s*(*br*) | 1.92 *s*(*br*) |

*$C_6D_6$ 1.98 *ddd*.

*J*(Hz): Compounds **18** and **20**: 2$\alpha$,2$\beta$ = 19; 2,3 = 4.5; 2',3 = 9.5; 3,4 = 1.5; 4,5 = 9; 4,5' = 3; 4,15 = 7; 5,5' = 15; 5,6 = 4; 5',6 = 7; 7,8 ~ 2; 7,13 = 2.5; 7,13' = 2; 8,9 = 8.5; 8,9' ~ 1; compound **21**: 2,3 = 16; 2,4 = 1.5; 3,4 = 4.5; 4,5 = 4; 4,5' = 6; 5,5' = 14; 5,6 = 2.5; 5',6 = 10; 6,7 = 2; 7,8 ~ 1.5; 8,9 = 8.5; 7,13 = 2.7; 7,13 = 2.5; compound **22**: 2,3 = 3,4 = 11; 4,5 = 11; 4,5' = 5; 4,15 = 7; 5,5' = 13; 5,6 = 5; 5',6 = 11; 6,7 ~ 1; 7,8 = 6.5; 7,13 = 1.5; 8,9 = 7.5; 9,9' = 14.

ing Δ-2,3-*cis*- and *trans*-isomeric angelates had been isolated previously[15]. Consequently, the $^1$H NMR spectral data were similar.

The overall picture of the chemistry of the genus *Lychnophora* looks very uniform. Obviously furanoheliangolides and related compounds are characteristic for the genus and large parts of the whole subtribe. So far these lactones have been isolated from *Eremanthus*[15], *Piptolepis*[16], *Proteopsis*[11] and *Vanillosmopsis*[16, 17] species, while *Chresta* contains glaucolides and hirsutinolides[18]. The monotypic genus *Albertinia*, however, afforded only lupeol and its acetate. These triterpenes are also present in all the other genera. The oxidized caryophyllene and α-humulene derivatives appear to be restricted to some *Lychnophora* species.

## EXPERIMENTAL

Air dried plant material, collected in north eastern Brazil, was extracted with $Et_2O$–petrol (1 : 2) and the resulting extracts were separated first by CC (Si gel) and further by repeated TLC (Si gel). Known compounds were identified by comparing the $^1$H NMR spectra with those of authentic material. Vouchers are deposited in the U.S. National Herbarium, Washington.

Lychnophora sellowii (*voucher RMK* 8479). The aerial parts (250 g) afforded 60 mg lupeol, 100 mg of its acetate, 3 mg *ent*-kaurene, 10 mg **1**, 20 mg **2**, 8 mg **5** ($Et_2O$–petrol, 3 : 1, several times), 3 mg **6** ($Et_2O$–petrol, 3 : 1, several times), 3 mg **10**, 3 mg **14**, 7 mg **15** ($Et_2O$–petrol, 1 : 1), 30 mg **16** and 0.2 mg **17**.

L. bahiensis (*voucher RMK* 8606). The aerial parts (460 g) afforded 500 mg lupenone, 200 mg lupeol, 5 mg squalene, 50 mg **1**, 2 mg **2**, 5 mg **3**, 100 mg **7**, 3 mg **8** ($Et_2O$–petrol, 3 : 1, several times), 1 mg **9** ($Et_2O$–petrol, 3 : 1, several times) and 2 mg **17**, while the roots (200 g) gave 300 mg lupenone, 100 mg lupeyl acetate, 50 mg lupeol, 2 mg dehydrocostus lactone, 10 mg **1**, 2 mg **3**, 5 mg **10**, 0.2 mg **17**.

L. crispa (*voucher RMK* 8618). The aerial parts (170 g) afforded 50 mg lupeol, 80 mg of its acetate, 4 mg **1**, 1 mg **4**, 5 mg **7**, 3 mg **8**, 12 mg **11**, 8 mg **12**, 5 mg **13** and 0.2 mg **17**, while the roots (60 g) gave 50 mg lupeol, 100 mg of its acetate, 1 mg **10** and 2 mg **17**.

L. blanchetii (*voucher RMK* 8151). The roots (150 g) afforded, in addition to compounds isolated previously, 3 mg **24** and 2 mg **25**, while the aerial parts (690 g) gave 8 mg **18** ($Et_2O$–petrol, 3 : 1), 2 mg **19**, 20 mg **20** ($Et_2O$–petrol, 3 : 1), 5 mg **21** ($Et_2O$–petrol, 3 : 1) and 40 mg **23**.

*5α - Hydroxy - 6α - angeloyloxy - Δ - 4,15 - isogoyazensanolide* (**5**). Colourless crystals, mp 172° ($Et_2O$), IR $\nu_{max}^{CHCl_3}$ cm$^{-1}$: 3610 (OH), 1770 (γ-lactone), 1720 (C=CCO), 1590 (C=C–OR); MS *m/z* (rel. int.): 374.137 $[M]^+$(1) ($C_{20}H_{22}O_7$), 356 $[M-H_2O]^+$(6), 330 $[M-CO_2]^+$(8), 274 $[M-RCO_2H]^+$(1), 83 $[C_4H_7CO]^+$(100), 55 $[83-CO]^+$(81);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365\,nm}{-43 \quad -45 \quad -45 \quad +25 \quad +1028} (CHCl_3;\ c = 1).$$

*5β - Hydroxy - 6α - angeloyloxy - Δ - 4,15 - isogoyazensanolide* (**6**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 3600 (OH), 1780 (γ-lactone), 1710 (C=CCO), 1590 (C=C–OR); MS *m/z* (rel. int.): 374.137 $[M]^+$(1)($C_{20}H_{22}O_7$), 356 $[M-H_2O]^+$(1), 274 $[M-RCO_2H]^+$(11), 83 $[C_4H_7CO]^+$(100), 55 $[83-CO]^+$(97).

*15 - Hydroxy - 16α - (1 - methylprop - 1Z - enyl) - eremanthanolide* (**8**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 3600 (OH), 1780 (γ-lactone), 1710 (C=CCO), 1585 (C=C–OR); MS *m/z* (rel. int.): 376.153 $[M]^+$(1)($C_{20}H_{24}O_7$), 358 $[M-H_2O]^+$(10), 83 $[C_4H_7CO]^+$(100), 55 $[83-CO]^+$(57);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365\,nm}{-20 \quad -21 \quad -20 \quad +39 \quad +581} (CHCl_3;\ c = 0.3).$$

*15 - Acetoxy - 16α - (1 - methylprop - 1Z - enyl) - eremanthanolide* (**9**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 3600 (OH), 1780 (γ-lactone), 1710 (C=CCO), 1585 (C=C–OR); MS *m/z* (rel. int.): 418 $[M]^+$(0.1), 400.152 $[M-H_2O]^+$(6), 358 $[M-HOAc]^+$(2), 83 $[C_4H_7CO]^+$(100), 55 $[83-CO]^+$(52).

*9-Oxo-bisabol-1-one* (**15**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 1670, 1620 (C=CCO); MS *m/z* (rel. int.): 234.162 $[M]^+$(7) ($C_{15}H_{22}O_2$), 219 $[M-Me]^+$(1), 137 $[M-CH_2COCH=CMe_2]^+$(78), 110 $[C_7H_{10}O]^+$(McLafferty)(88), 83 $[C_4H_7CO]^+$(100), 55 $[83-CO]^+$(48); $[\alpha]_D = +20°$ ($CHCl_3$; *c* = 0.3).

*3β - Methoxy - 8 - desacyl - 2,3 - dihydroereglomerulide - 8 -O -methacrylate* (**18**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 1775 (γ-lactone), 1720 (C=$CCO_2R$); MS *m/z* (rel. int.): 390.168 $[M-MeOH]^+$(1)($C_{21}H_{26}O_7$), 380 $[M-ketene]^+$(10), 362 $[M-HOAc]^+$(4), 347 $[362-Me]^+$(25), 330 $[362-MeOH]^+$(3), 82 $[O=C=CH-CH=CHMe]^+$(97), 69 $[C_3H_5CO]^+$(100).

*3β - Hydroxy - 8 - desacyl - 2,3 - dihydroereglomerulide - 8 - O - methacrylate* (**20**). Colourless gum, IR $\nu_{max}^{CHCl_3}$ cm$^{-1}$: 3540 (OH), 1770 (lactone), 1745 (OAc), 1725 (C=O, $C=CCO_2R$); MS *m/z* (rel. int.): 340.168 $[M-H_2O]^+$(3) ($C_{21}H_{26}O_7$), 362 $[390-CO]^+$(6), 347 $[362-Me]^+$(25), 82 $[O=C=CH-CH=CHMe]^+$(46), 69 $[C_3H_5CO]^+$(100).

10 mg **20** on heating with 100 mg $Ac_2O$ for 1 hr at 70° afforded 6 mg **21** and 1 mg **22** [separated by HPLC (reversed phase, MeOH–$H_2O$, 3 : 2)], colourless gum, IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 1775 (lactone), 1740, 1245 (OAc), 1720, 1650 (C=$CCO_2R$), 1720, 1620 (C=CCO); MS *m/z* (rel. int.): 390.168 $[M]^+$(1)($C_{21}H_{26}O_7$), 362 (1), 347 (22), 251 (21), 82 (93), 69 (100).

*8 - Desacyl - 2,3 - trans - ereglomerulide - 8 - O - methacrylate* (**21**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 1775 (lactone), 1745, 1240 (OAc), 1720 (C=$CCO_2R$), 1720, 1625 (C=CCO); MS *m/z* (rel. int.): 390.168 $[M]^+$(3)($C_{21}H_{26}O_7$), 362 $[M-CO]^+$(1), 347 $[362-Me]^+$(24), 251 $[347-HO_2CR]^+$(25), 82 $[O=C=CH-CH=CHMe]^+$(97), 97 $[C_3H_5CO]^+$(100).

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