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TRICYCLIC SESQUITERPENES AND FURTHER DITERPENES FROM *ESPELETIOPSIS* SPECIES*

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Key Word Index—*Espeletiopsis guacharaca*; *E. glandulosa*; *E. garciae*; *E. purpurascens*; *E. tachirensis*; *Coespeletia marcana*; *C. moritziana*; Compositae; Heliantheae; new sesquiterpene ketones; new *ent*-kaurene derivatives.

Abstract—The investigation of five *Espeletiopsis* and two *Coespeletia* species afforded, in addition to numerous known compounds, two new kaurene derivatives 19-acetoxy-*ent*-kaurene and 17-oxo-*ent*-kaur-15-en-19-oic acid, as well as two new tricyclic sesquiterpenes, one being the previously reported oxidation product of copaborneol and the second one the 5-oxo derivative of silphiperfol-6-ene. The structures were elucidated by NMR studies and by chemical transformations. The chemotaxonomic situation is discussed briefly.

INTRODUCTION

The genus *Espeletiopsis* is one of the new genera of the former large genus *Espeletia*, now being separated into several new genera [1]. Though some results on related genera are already reported [2, 3], so far nothing is known about the chemistry of this genus. We have now studied the stems of five species. All of them contain large amounts of *ent*-kaurene derivatives, two of them being previously unknown. From one species copaborneol, copacamphor and a new keto derivative of silphiperfol-6-ene were obtained. The structure of the latter compound was established by partial synthesis, while that of copacamphor, not isolated before, was confirmed by transformation of copaborneol to the ketone, which on reduction afforded the isomeric alcohol. Two *Coespeletia* species only yielded known compounds.

RESULTS AND DISCUSSION

The stems of *Espeletiopsis guacharaca* (Diaz) Cuatr. afforded *ent*-kaurenic acid (**9**), grandifloric acid (**15**) [4], grandifloric acid acetate (**10**) [4], the isovalerate (**11**) [3], 9β-hydroxy-grandifloric acid isovalerate (**12**) (F. Bohlmann and C. Zdero, unpublished results), *ent*-kaur-9(11),16(17)-dien-19-oic acid (**17**) [5], the corresponding 12β-hydroxy- and 12-oxo derivatives (**18**) [6], **19** [6], 17-hydroxy-*ent*-kaur-15(16)-en-19-oic acid (**21**) [3], *ent*-kaurene (**1**), 18- and 19-nor-*ent*-kaurene (**2**) [2], (**3**) [2], 19-oxo-*ent*-kaurene (**8**) [7], 19-hydroxy-*ent*-kaurene (**6**) [7], ruilopezol (**5**) [3] and 16α-hydroxy-*ent*-kaurene (**24**) [8]. Furthermore, manoyloxide (**25**) [9], caryophyllenepoxide (**28**) [10], α-pinene (**31**), verbenone (**32**), verbenol (**33**) and (+)-copaborneol (**37**) [11] were isolated. In addition two diterpenes, not isolated before, were present. The first one was an acetate, its ^{1}H NMR data (Table 1) showed that a kaurene derivative was present. The molecular formula ($C_{22}H_{34}O_2$) indicated a simple acetoxy kaurene. The two doublets at δ 4.79 and 4.73 (J = 11 Hz) were in agreement with an 18, 19- or 20-acetoxy-kaurene. The chemical shifts already indicated a 19-position (**7**), which was established by acetylation of **6** to afford the same acetate **7**. The second diterpene was an aldehyde (9.74, *s*). The ^{1}H NMR data were very similar to those of **21** (Table 1) except for a drastic downfield shift of the olefinic proton signal (6.57, *d*, J = 0.8 Hz) and a moderate shift of the 13-H signal. Manganese dioxide oxidation of **21** afforded the aldehyde **22** which was identical with the natural product.

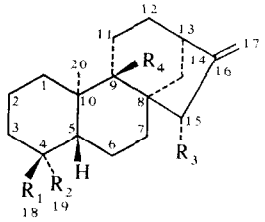
The neutral fraction further contained two sesquiterpene ketones. The less polar one, molecular formula $C_{15}H_{24}O$, was a tricyclic compound, which had no olefinic carbons as could be seen from the ^{1}H NMR data (Table 2). However, the spectrum in $CDCl_3$, did not show if there were two secondary methyls on different carbons or if an isopropyl group was present. In C_6D_6 the methyl signals were separated and double resonance showed that an

Table 1. ^{1}H NMR spectral data of compounds **7** and **23** (270 MHz)

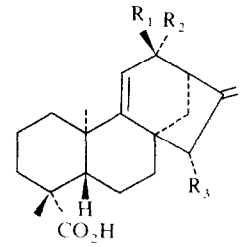
	7	**23***
13-H	2.65 *m*	3.05 *m*
17-H	4.79 *s(br.)*	9.74 *s*
17′-H	4.73 *s(br.)*	
18-H	1.04 *s*	1.18 *s*
19-H	4.23 *d*	—
19′-H	3.89 *dd*	—
20-H	0.95 *s*	0.88 *s*
OAc(CO_2Me)	2.05 *s*	3.66 *s*

J(Hz): **7**: 19, 19′ = 11; 18, 19′ = 1.
* 15-H 6.57 *d* (J = 0.8 Hz).

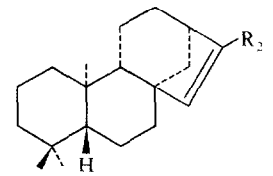
* Part 286 in the series "Naturally Occurring Terpene Derivatives". For Part 285 see Bohlmann, F., Grenz, M., Gupta, R. K., Dhar, A. K., Ahmed, M., King, R. M. and Robinson, H. (1980) *Phytochemistry* **19**, in press.



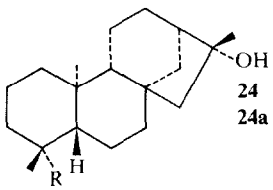
	R_1	R_2	R_3	R_4
1	Me	Me	H	H
2	H	Me	H	H
3	Me	H	H	H
4	OH	Me	H	H
5	Me	OH	H	H
6	Me	CH_2OH	H	H
7	Me	CH_2OAc	H	H
8	Me	CHO	H	H
9	Me	CO_2H	H	H
10	Me	CO_2H	OAc	H
11	Me	CO_2H	OiVal	H
12	Me	CO_2H	OiVal	OH
13	Me	CO_2H	OSen	H
14	Me	CO_2H	OSen	OH
15	Me	CO_2H	OH	H
16	Me	CO_2H	OiBu	H



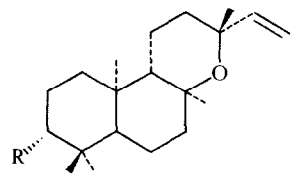
	R_1	R_2	R_3
17	H	H	H
18	OH	H	H
19		=O	H
20	H	H	OH



	R_1	R_2	CO_2R_1
21	H	CH_2OH	
22	H	CHO	
23	Me	CHO	



24 R = Me
24a R = CO_2H



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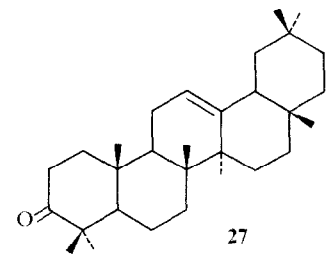
26 R = OH



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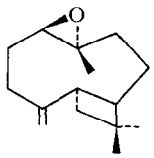

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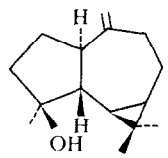

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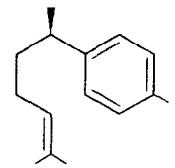

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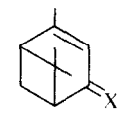
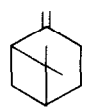


31 X = H_2
32 X = O
33 X = OH,H



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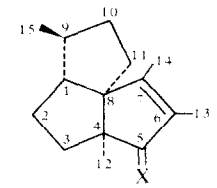
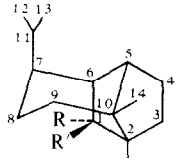


35 X = O
36 X = H_2



	37	**38**	**39**	**40**
R	OH	OAc	=O	H
R′	H	H		OH

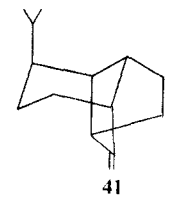


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Table 2. ^{1}H NMR spectral data of compounds **37**–**40** (270 MHz)

	37 C_6D_6	+ Eu(fod)$_3$	**38**(C_6D_6)	**39**($CDCl_3$)	**40**($CDCl_3$)
1-H	3.33 *s(br.)*	11.04 *s(br.)*	4.64 *s(br.)*	—	3.63 *d* (J = 8 Hz)
3α-H	2.06 *ddd*	6.86 *ddd*	2.04 *ddd*		
3β-H	1.27 *m*	2.3 *m*			
4α-H	1.71	4.04 *m*	1.73 *m*		
4β-H	1.35 *m*	3.50 *m*			
5-H	1.54 *d*	3.29 *d*	1.60 *d*	1.99 *d*	
6-H	1.40 *s(br.)*	6.57 *s(br.)*	1.53 *s(br.)*	2.17 *d(br.)*	
11-H	1.27 *m*	2.3 *m*	1.15 *m*		
12-H	0.96 *d*	1.38 *d*	1.60 *d*	0.92 *d*	0.91 *d*
13-H	0.92 *d*	1.25 *d*	0.94 *d*	0.89 *d*	0.90 *d*
14-H	0.85 *s*	1.95 *s*	0.94 *s*	0.95 *s*	0.88 *s*
15-H	0.89 *s*	3.13 *s*	0.82 *s*	0.89 *s*	0.79 *s*
OAc	—	—	1.76 *s*	—	—

J (Hz): **37**: 3α, 3β = 12; 3α, 4α = 5; 3α, 4β = 10; 4β, 5 = 5; 11, 12 = 11, 13 = 6.5.

isopropyl group must be present. All other data agreed with copacamphor (**39**) [11, 12]. The corresponding alcohol, copaborneol (**37**), [12] was also isolated, though the identification was difficult as there is some confusion in the literature [11, 12] concerning the optical rotation of these compounds. Therefore we prepared the acetate **38** and by oxidation with pyridine chlorochromate obtained the corresponding ketone **39** [11], which was identical with the isolated ketone. Reduction of the latter afforded the epimeric alcohol **40** [11]. Furthermore, **37** was transformed to copacamphene (**41**) [11], which had the same optical rotation as that reported in the literature [11]. The ^{1}H NMR data (Table 2) of these compounds were fully in agreement with the proposed structures. The ^{13}C NMR data of the acetate **38** further supported the structures (see Experimental).

The second ketone, molecular formula $C_{15}H_{22}O$, was a tricyclic compound, which, however, possessed a double bond, as was shown by the ^{13}C NMR data (Table 3). The keto group was conjugated (IR 1695 cm^{-1}). The ^{1}H NMR spectrum (Table 3) only showed the presence of two olefinic methyls as well as a tertiary and a secondary methyl. Though the other signals could not be interpretated directly, the similarity with those of silphiperfol-6-ene (**36**) [13] indicated that the new ketone may be the 5-oxo derivative of **36**. Indeed, oxidation of **36** with pyridine chlorochromate afforded a ketone, which was identical with the natural compound, confirming this proposal. Compound **35** is the first derivative of the unusual hydrocarbon **36**, so far isolated only from *Silphium* species [13].

The stems of *E. glandulosa* Cuatr. also contained **5**, **6**, **9**–**11**, **15**, **17** and **19** as well as 15α-senecioyloxy-*ent*-kaurenic acid (**13**) [3], while those of *E. garciae* Cuatr. again afforded **6**, **9**–**11**, **13** and **17**. The stems of *E. pupurascens* Cuatr. also contained **1**–**3**, **5**, **6**, **9**, **10**, **13**, **17**–**19**, **21**, **24**, 4-epiruilopezol (**4**) [3] and 15α-isobutyryloxy-*ent*-kaurenic acid (**16**) [14], while those of *E. tachirensis* (Aristeg.) Cuatr. afforded **4**–**6**, **9**, **10**, **13**, **15**, **17**–**19**, **21**, **24**, 9β-hydroxy-15α-senecioyloxy-*ent*-kaurenic acid (**14**) [3] and 9,11-dehydrograndifloric acid (**20**) [3].

The stems of *Coespeletia marcana* Cuatr. contained **1**–**6**, **8**–**10**, **15**, **18**, **19**, **21**, **24**, **32**, **33**, 16-α-hydroxy-kauren-19-oic acid (**24a**) [15], and spathulenol (**29**) [17], while from the stems of *C. moritziana* (Sch. Bip.) Cuatr. **2**, **3**, **5**, **6**, **8**, **9**–**11**, **13**, **17**, **22**, **25**, **29**, **32**, **33**, 3α-hydroxy-13-*epi*-manoyloxide (**26**) [3], amyrone (**27**), curcumene (**30**) and β-pinene (**34**) were isolated. The leaves also contained **6**, **8**, **9**–**11**, **13**, **17**, **21**, **22** and **26**.

So far the overall picture of the chemistry of the subtribe Espeletiinae is more or less uniform [2,3]. All genera are characterized by the occurrence of large amounts of kaurene derivatives, only the degree of variation and the concentrations are different. The picture of the sesquiterpenes isolated up to now is not very characteristic, though the occurrence of large amounts of spathulenol in both

Table 3. ^{1}H NMR and ^{13}C NMR spectral data of compound **35** ($CDCl_3$)

^{1}H NMR		^{13}C NMR			
3β-H	2.02 *ddd*	C-1	57.9 *d*	C-9	39.6 *d*
12-H	1.01 *s*	C-2	28.9 *t*	C-10	35.2 *t*
13-H	1.98 *q*	C-3	36.7 *t*	C-11	26.1 *t*
14-H	1.68 *q*	C-4	58.0 *s*	C-12	21.1 *q*
15-H	1.01 *d*	C-5	213.9 *s*	C-13	8.3 *q*
		C-6	133.4 *s*	C-14	13.0 *q*
		C-7	173.3 *s*	C-15	19.1 *q*
		C-8	67.3 *s*		

J (Hz): 2, 3β = 4, 5; 3α, 3β = 12.5; 13, 14 = 1.

Coespeletia species is remarkable. Further investigations, probably with fresh plant material of *Espeletiopsis* species, may indicate whether the unusual sesquiterpenes **35**, **37** and **38** are characteristic of this genus.

EXPERIMENTAL

^{1}H NMR: 270 MHz, TMS as int. standard; optical rotation: $CHCl_3$; MS: 70 eV, direct inlet. The air-dried stems (collected in Venezuela) were chopped and extracted with Et_2O–petrol (1:2). The extracts obtained were separated first by CC (Si gel, act. grade II). The acid fraction was separated as its methyl esters (by reaction with CH_2N_2). Final purification was done by TLC (Si gel, GF 254). In most cases only part of the fractions (not more than 0.5 g) was separated completely by TLC. The given amounts of isolated compounds are therefore calculated only. Known compounds were identified by comparison of the optical rotations, the IR and ^{1}H NMR spectra with those of authentic material.

Espeletiopsis guacharaca (*voucher Cuatr.* 28697). The stems (450 g) afforded 20 mg **1**, 30 mg **2**, 30 mg **3**, 80 mg **5**, 860 mg **6**, 35 mg **7** (Et_2O–petrol, 1:10), 50 mg **8**, 1.8 g **9**, 960 mg **10**, 2.5 g **11**, 800 mg **12**, 480 mg **15**, 240 mg **17**, 600 mg **18**, 240 mg **19**, 720 mg **21**, 800 mg **22** [isolated as its methyl ester **23** (Et_2O–petrol, 1:3)], 70 mg **24**, 30 mg **25**, 60 mg **28**, 80 mg **31**, 340 mg **32**, 270 mg **33**, 150 mg **35** (Et_2O–petrol, 1:10), 130 mg **37**, (Et_2O–petrol, 1:1) and 8 mg **39** (Et_2O–petrol, 1:10).

Espeletiopsis glandulosa (*voucher Cuatr.* 27744). The stems (230 g) afforded 20 mg **5**, 80 mg **6**, 390 mg **9**, 160 mg **10**, 700 mg **11**, 100 mg **13**, 20 mg **15**, 390 mg **17** and 20 mg **19**.

Espeletiopsis garciae (*voucher Cuatr.* 28660). The stems (250 g) gave 15 mg **6**, 40 mg **9**, 25 mg **10**, 15 mg **11**, 20 mg **13** and 10 mg **17**.

Espeletiopsis purpurascens (*voucher Cuatr.* 28325). The stems (500 g) afforded 10 mg **1**, 20 mg **2**, 20 mg **3**, 150 mg **4**, 150 mg **5**, 600 mg **6**, 450 mg **9**, 14 mg **10**, 10 mg **13**, 10 mg **16**, 90 mg **17**, 250 mg **18**, 200 mg **19**, 200 mg **21** and 50 mg **24**.

Espeletiopsis tachirensis (*voucher Cuatr.* 28418). The stems (500 g) afforded 25 mg **4**, 5 mg **5**, 30 mg **6**, 175 mg **9**, 15 mg **10**, 35 mg **13**, 5 mg **14**, 15 mg **15**, 50 mg **17**, 20 mg **18**, 10 mg **19**, 15 mg **20**, 35 mg **21** and 10 mg **24**.

Coespeletia marcana (*voucher Cuatr.* 28376). The stems (450 g) afforded 10 mg **1**, 20 mg **2**, 20 mg **3**, 10 mg **4**, 50 mg **5**, 200 mg **6**, 150 mg **8**, 300 mg **9**, 180 mg **10**, 180 mg **15**, 90 mg **18**, 60 mg **19**, 150 mg **21**, 15 mg **24**, 60 mg **24a**, 80 mg **29**, 30 mg **32** and 15 mg **33**.

Coespeletia moritziana (*voucher Cuatr.* 28628). The stems (700 g) gave 30 mg **2**, 30 mg **3**, 300 mg **5**, 500 mg **6**, 450 mg **8**, 10 g **9**, 1 g **10**, 2 g **11**, 5 g **13**, 5 g **17**, 200 mg **22**, 400 mg **25**, 1.5 g **26**, 160 mg **27**, 180 mg **29**, 60 mg **30**, 450 mg **32**, 300 mg **33** and 30 mg **34** while the leaves (600 g) afforded 1.7 g **6**, 0.8 g **8**, 3.8 g **9**, 2.5 g **10**, 0.8 g **11**, 4.5 g **13**, 0.8 g **17**, 0.8 g **21**, 1.5 g **22** and 1.5 g **26**.

19-*Acetoxy*-ent-*kaurene* (**7**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740, 1250 (OAc), 885 (=CH_2); MS *m/e* (rel. int.): 330.256 M$^+$, (15) ($C_{22}H_{34}O_2$), 315 (4) (M − ·Me), 288 (4) (M − ketene), 270 (6) (M − HOAc), 255 (10) (270 − ·Me), 43 (100) ($MeCO^+$).

$$[\alpha]_{24}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-25.5 \quad -26.0 \quad -29.2 \quad -48.0} \quad (c = 1.5).$$

Compound **6** (20 mg) was heated for 3 hr with 0.5 ml Ac_2O at 70°. TLC afforded 21 mg **7**, identical with the natural compound.

17-*Oxo*-ent-*kaur*-15(16)-*en*-19-*oic acid* (**22**). Isolated as its methyl ester (**23**), colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1730, 1165 (CO_2Me, axial), 2720, 1680, 1605 (C=CCHO); MS *m/e* (rel. int.): 330.218 M$^+$, (90) ($C_{21}H_{30}O_3$), 315 (41) (M − ·Me), 299 (20) (M − ·OMe), 271 (70) (M − ·CO_2Me), 270 (50) (M − HCO_2Me), 255 (60) (270 − ·Me), 91 (100) ($C_7H_7^+$).

$$[\alpha]_{24}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-68 \quad -70 \quad -78 \quad -88} \quad (c = 0.5).$$

The methyl ester of **21** (20 mg) in 3 ml Et_2O was stirred for 3 days with 200 mg MnO_2. TLC (Et_2O–petrol, 1:3) afforded 15 mg **23**, IR and ^{1}H NMR spectra identical with those of the methyl ester of **22**.

5-*Oxo*-*silphiperfol*-6-*ene* (**35**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1695, 1645 (C=CCO); MS *m/e* (rel. int.): 218.162 M$^+$ (76) ($C_{15}H_{22}O$), 203 (18) (M − ·Me), 190 (13) (M − CO), 175 (19) (203 − CO), 163 (47) (M − C_4H_7), 136 (100) (M − COC(Me)C=C).

$$[\alpha]_{24}^{\lambda} \pm = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-40.0 \quad -41.8 \quad -47.3 \quad -78.5} \quad (c = 1.3).$$

Synthesis of **35**. Compound **36** (10 mg) in 2 ml $CHCl_3$ was stirred for 3 days with 20 mg pyridine chlorochromate. TLC (Et_2O–petrol, 1:20) afforded 8 mg **35**, identical with the natural ketone.

Copaborneol (**37**). Colourless oil, ^{1}H NMR see Table 2.

$$[\alpha]_{24}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+9.0 \quad +9.5 \quad +10.9 \quad +16.5} \quad (c = 1.3).$$

(+)-*Copacamphor* (**39**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1742 (CO); MS *m/e* (rel. int.): 220.183 M$^+$, (58) ($C_{15}H_{24}O$), 177 (23) (M − C_3H_7), 149 (36) (177 − CO), 124 (100) ($C_9H_{16}^+$), 95 (51) ($C_7H_{11}^+$).

$$[\alpha]_{24}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+111 \quad +117 \quad +137 \quad +174} \quad (c = 0.8).$$

Compound **37** (20 mg) in 2 ml CH_2Cl_2 was stirred 2 hr with 20 mg pyridine chlorochromate yielding 15 mg **39**, identical with the natural ketone. 50 mg **37** was heated for 1 hr with 0.1 ml Ac_2O. TLC (Et_2O–petrol, 1:10) afforded 40 mg **38**, colourless oil: ^{1}H NMR see Table 2; ^{13}C NMR ($CDCl_3$): (C-1 through C-15): δ 87.8 *d*, 49.4 *s*, 24.9 *t*, 29.1 *t*, 41.6 *d*, 47.7 *d*, 49.9 *d*, 23.5 *t*, 27.4 *t*, 48.9 *s*, 31.8 *d*, 20.6 *q*, 20.4 *t*, 13.6 *q*, 19.3 *q*, 21.2 *q*, 171.3 *s* (OAc). (Assignments not really established, but in agreement with the usual shift-rules.) 10 mg **39** on reduction with $LiAlH_4$ (10 mg, Et_2O, 5 min, room temp.) afforded after TLC (Et_2O–petrol, 1:3) 8 mg **40**, colourless oil: ^{1}H NMR see Table 2. 10 mg **37** was reacted with 0.1 ml pyridine and 50 mg thionylchloride (0°, 1 hr). TLC afforded 5 mg **41**, spectral data in agreement with those reported in the lit. [11].

$$[\alpha]_{24}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-168 \quad -175 \quad -202 \quad -369} \quad (c = 0.3)$$

(lit. [11] $[\alpha_D]$ −159°).

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