

Supplementary Information

Figure S1. IR spectrum of hydroxysafflor yellow B (1).

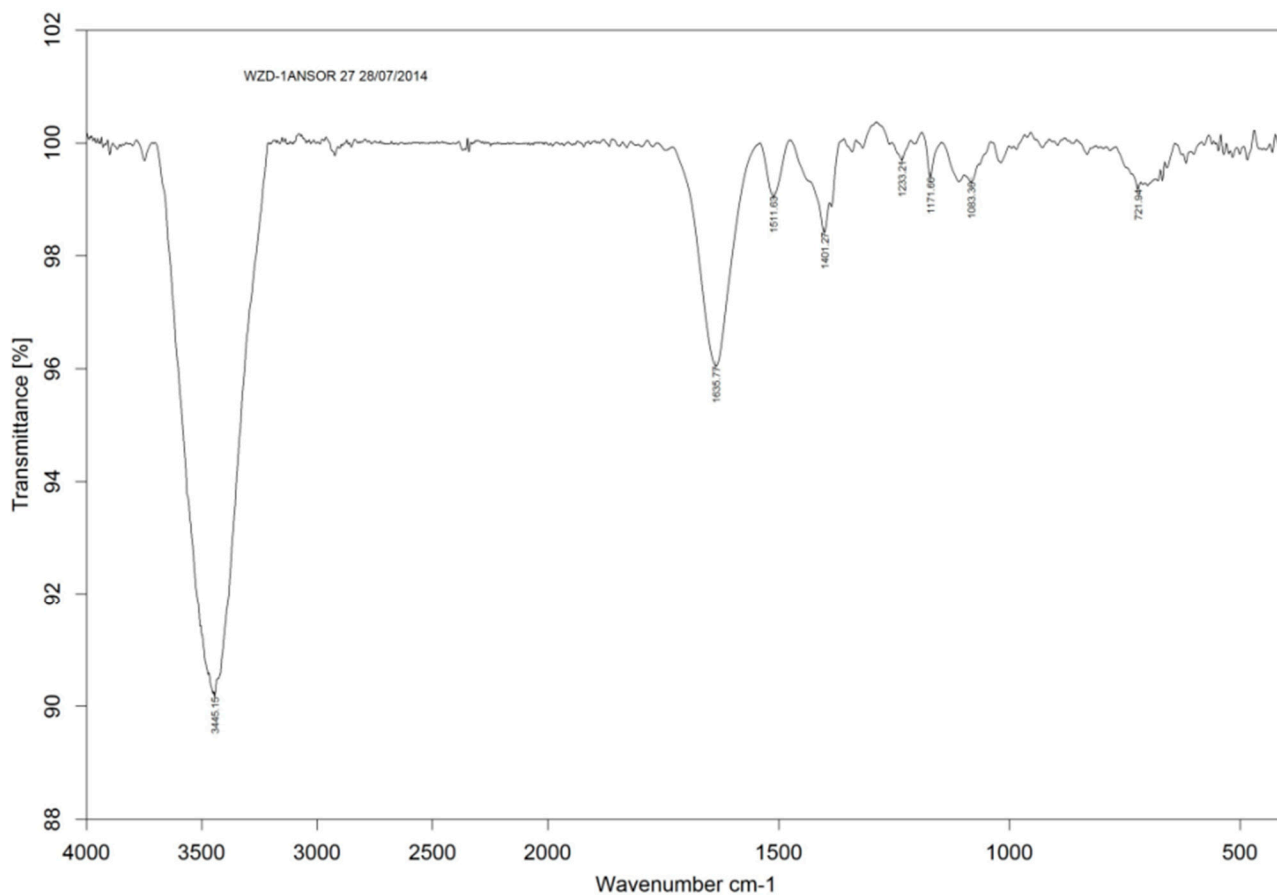


Figure S2. ESI spectrum of hydroxysafflor yellow B (1) in MeOH.

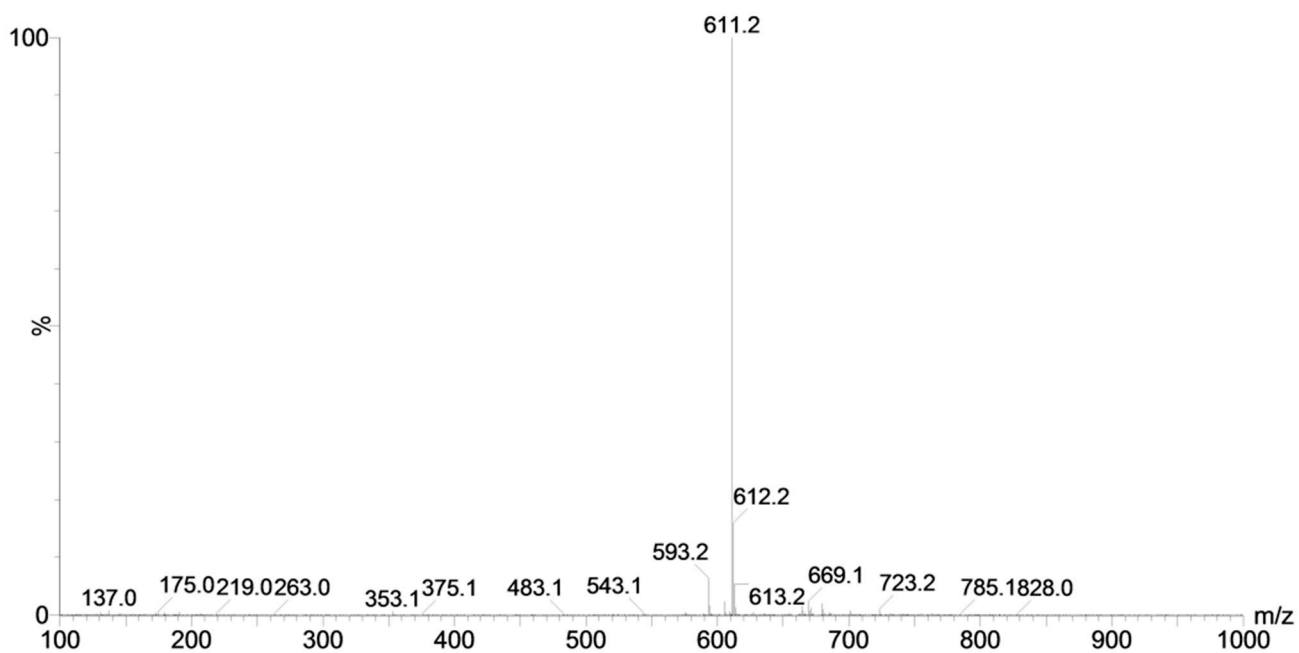


Figure S3. HRESIMS spectrum of hydroxysafflor yellow B (1) in MeOH.

Monoisotopic Mass, Odd and Even Electron Ions

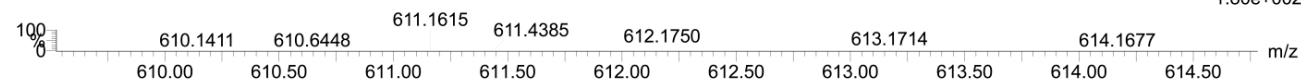
186 formula(e) evaluated with 2 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 0-500 H: 0-1000 O: 0-200

1

leshijun_140812_5 71 (2.176)

2: TOF MSMS 611.00ES-
1.80e+002

Minimum: 80.00
Maximum: 100.00

Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
611.1615	100.00	611.1612	0.3	0.5	12.5	12.9	0.044	95.71	C27 H31 O16
		611.1647	-3.2	-5.2	34.5	16.0	3.150	4.29	C45 H23 O3

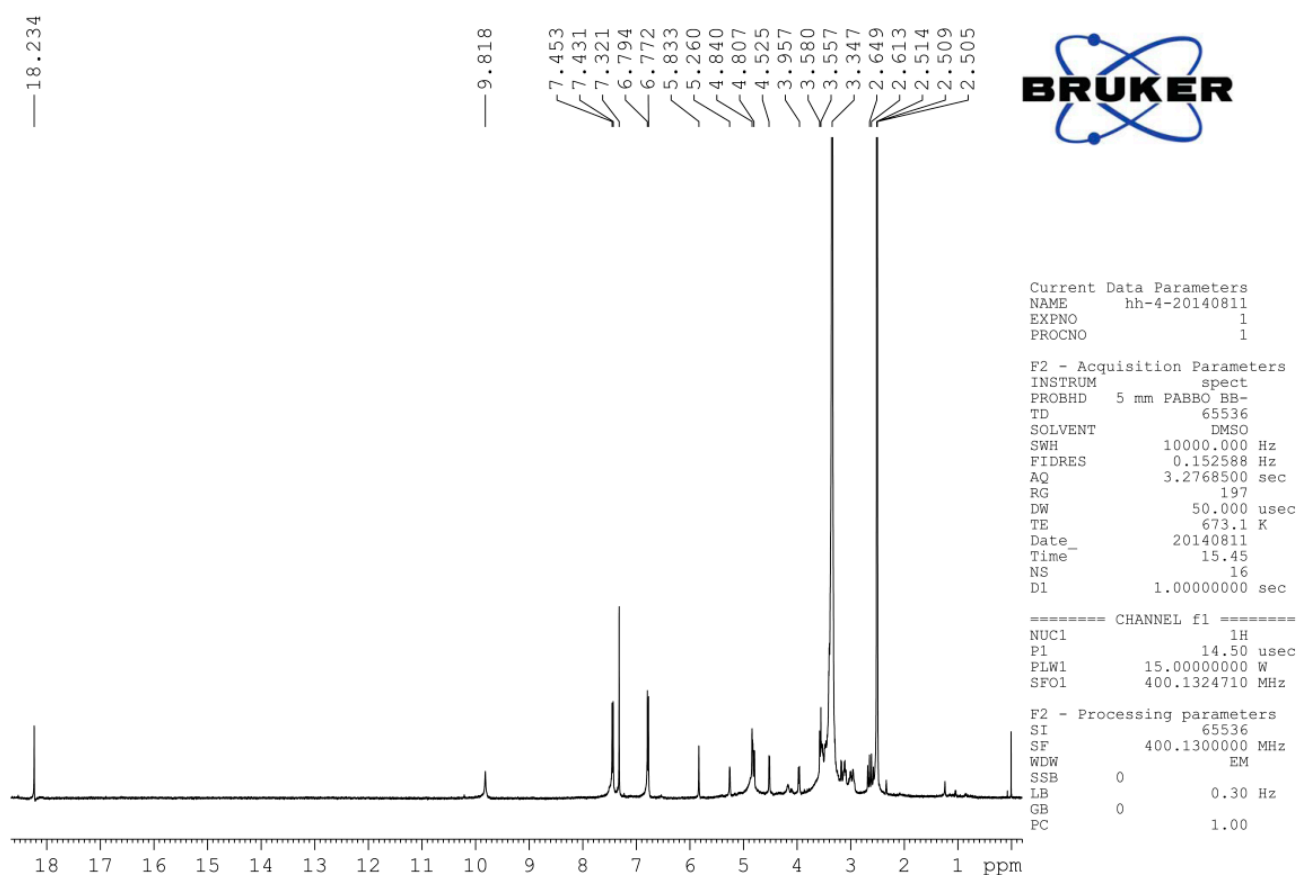
Figure S4. ¹H-NMR spectrum of hydroxysafflor yellow B (1) in DMSO-*d*₆.

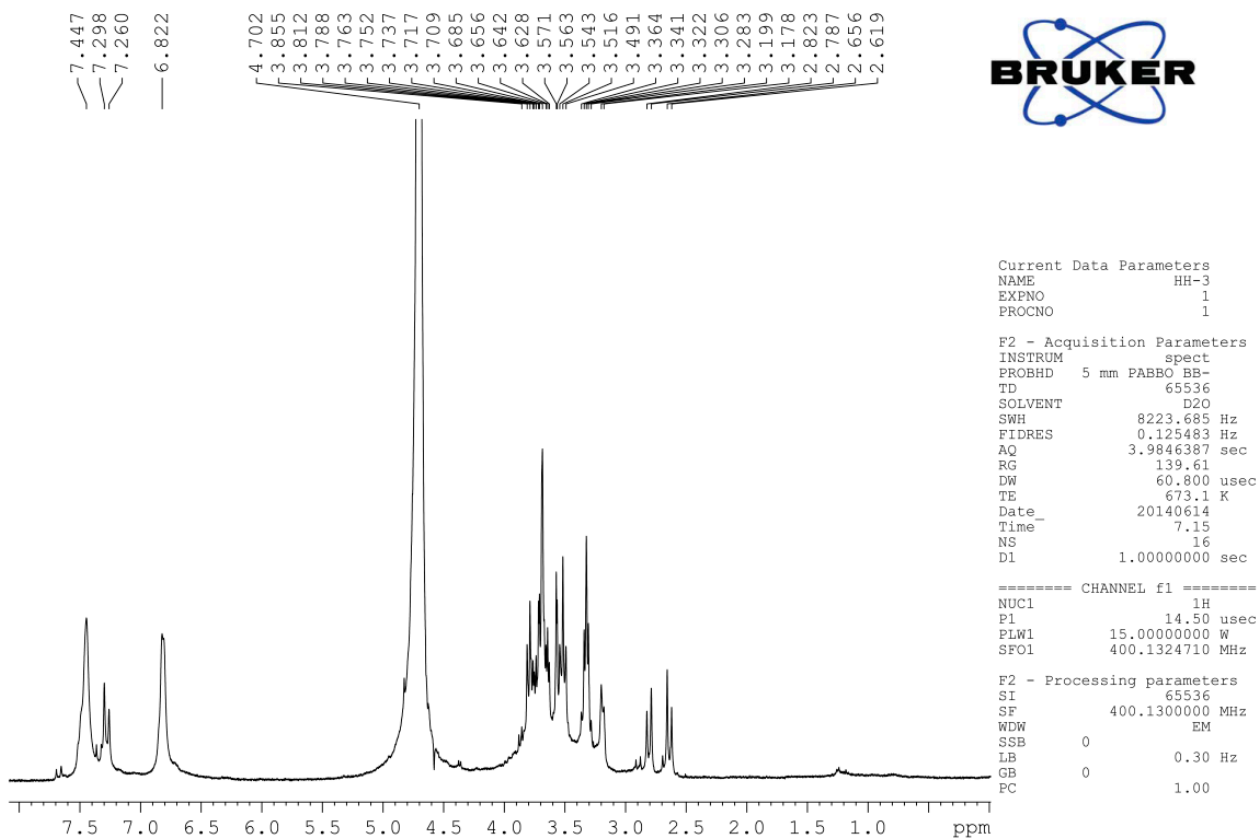
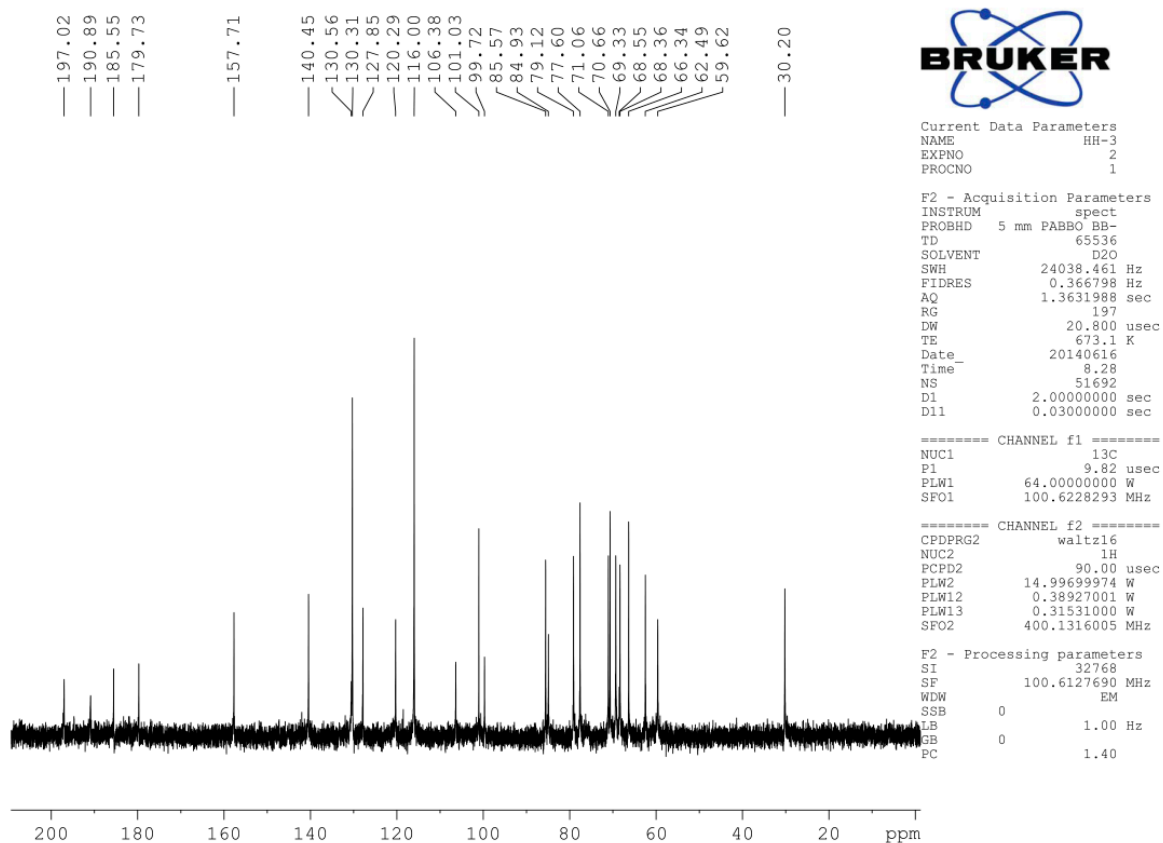
Figure S5. ^1H -NMR spectrum of hydroxysafflor yellow B (1) in D_2O .Figure S6. ^{13}C -NMR spectrum of hydroxysafflor yellow B (1) in D_2O .

Figure S7. HSQC NMR spectrum of hydroxysafflor yellow B (1) in D₂O.

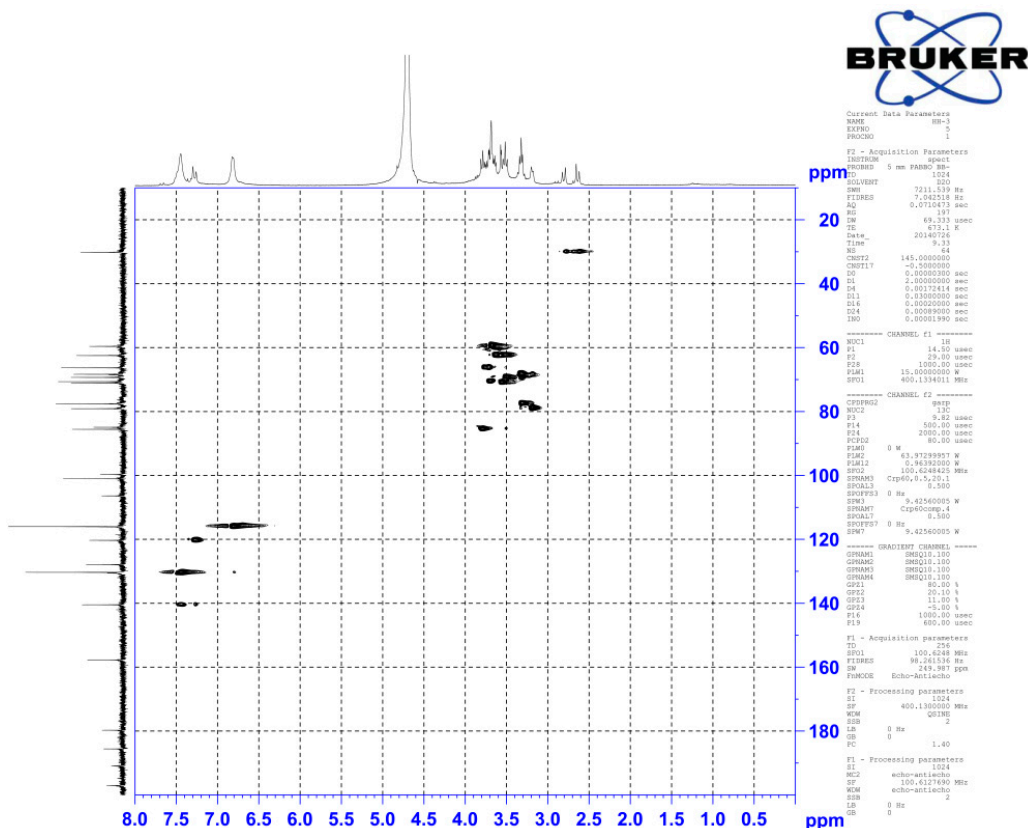


Figure S8. HMBC NMR spectrum of hydroxysafflor yellow B (1) in D₂O.

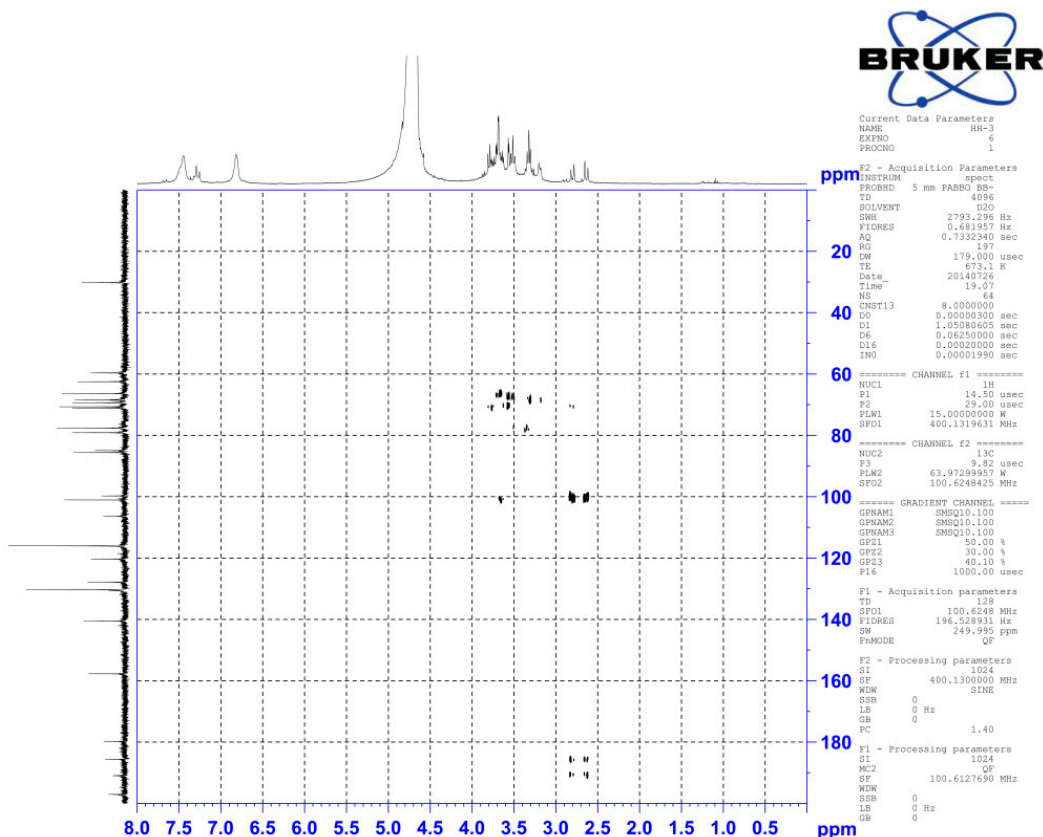


Figure S9. COSY NMR spectrum of hydroxysafflor yellow B (1) in D₂O.

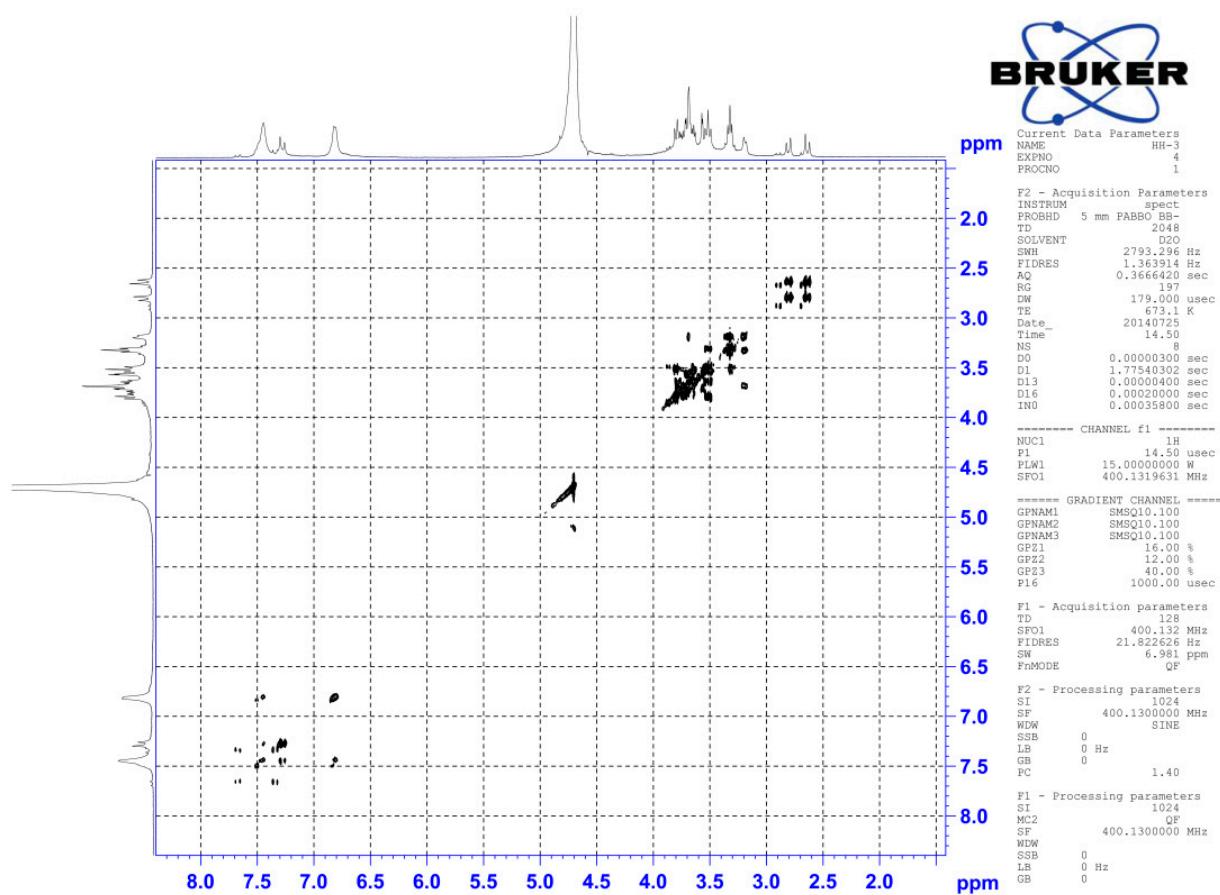


Figure S10. IR spectrum of hydroxysafflor yellow C (2)

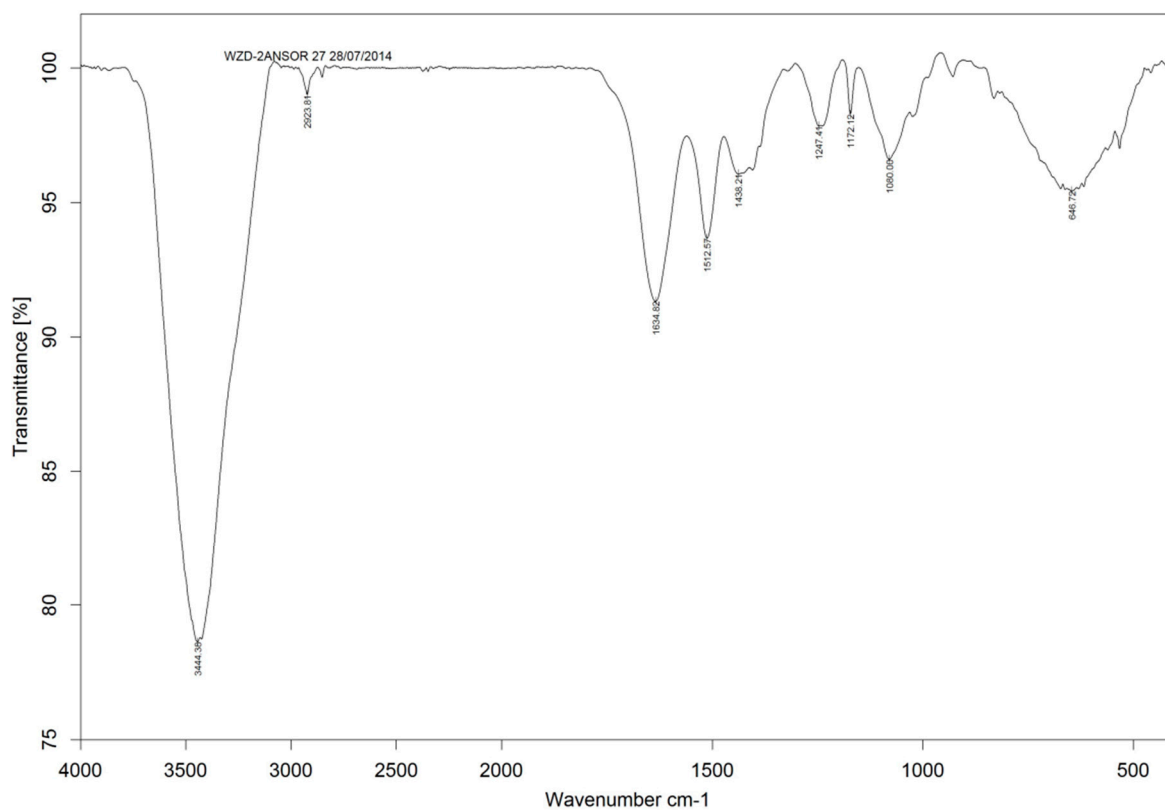
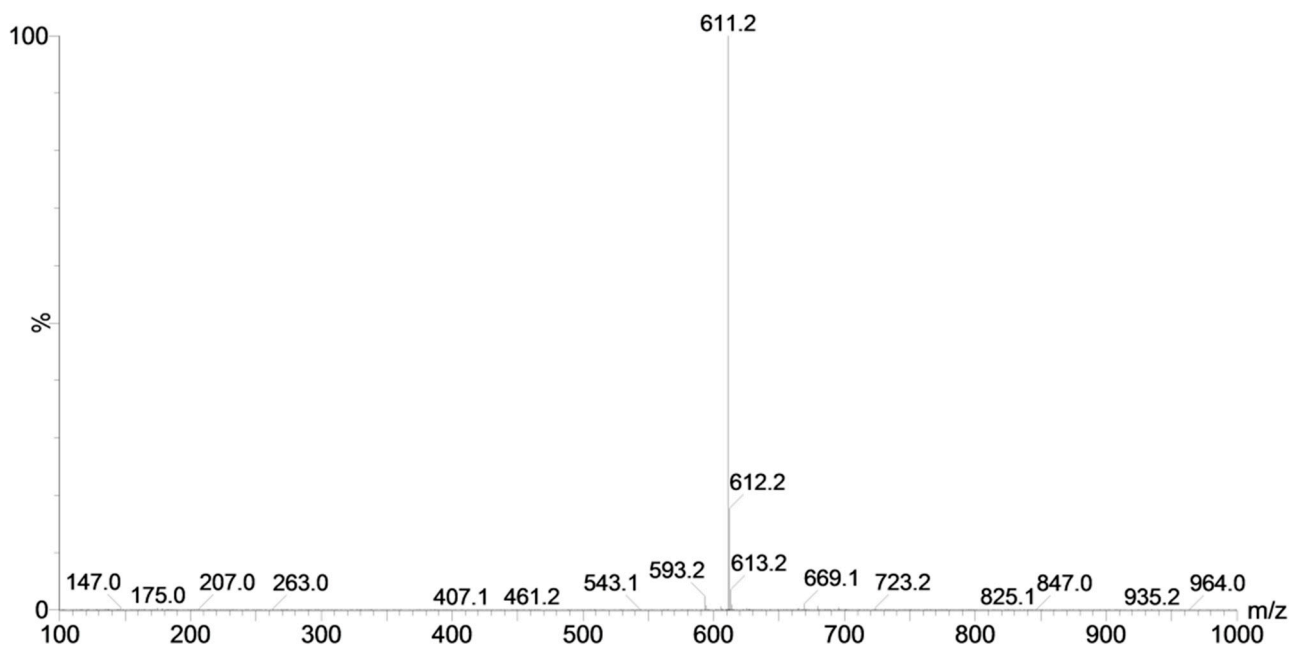


Figure S11. ESI spectrum of hydroxysafflor yellow C (2) in MeOH.**Figure S12.** HRESIMS spectrum of hydroxysafflor yellow C (2) in MeOH.

Monoisotopic Mass, Odd and Even Electron Ions

186 formula(e) evaluated with 3 results within limits (up to 50 best isotopic matches for each mass)

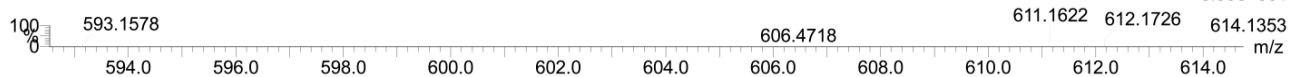
Elements Used:

C: 0-500 H: 0-1000 O: 0-200

2

leshijun_140812_6 70 (2.148)

2: TOF MSMS 611.00ES-
8.90e+001



Minimum: 80.00 -1.5
Maximum: 100.00 5.0 10.0 50.0

Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
611.1622	100.00	611.1612	1.0	1.6	12.5	10.0	0.716	48.88	C27 H31 O16
		611.1671	-4.9	-8.0	3.5	10.3	1.087	33.72	C20 H35 O21
		611.1647	-2.5	-4.1	34.5	11.0	1.748	17.41	C45 H23 O3

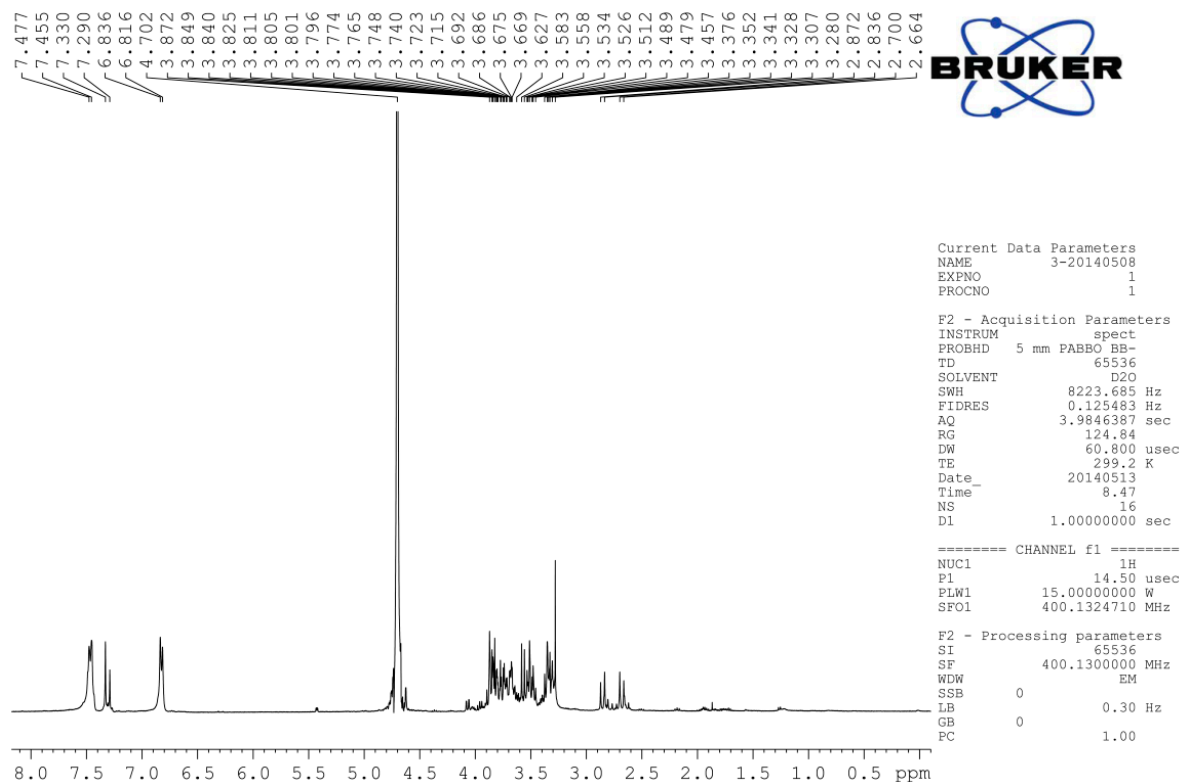
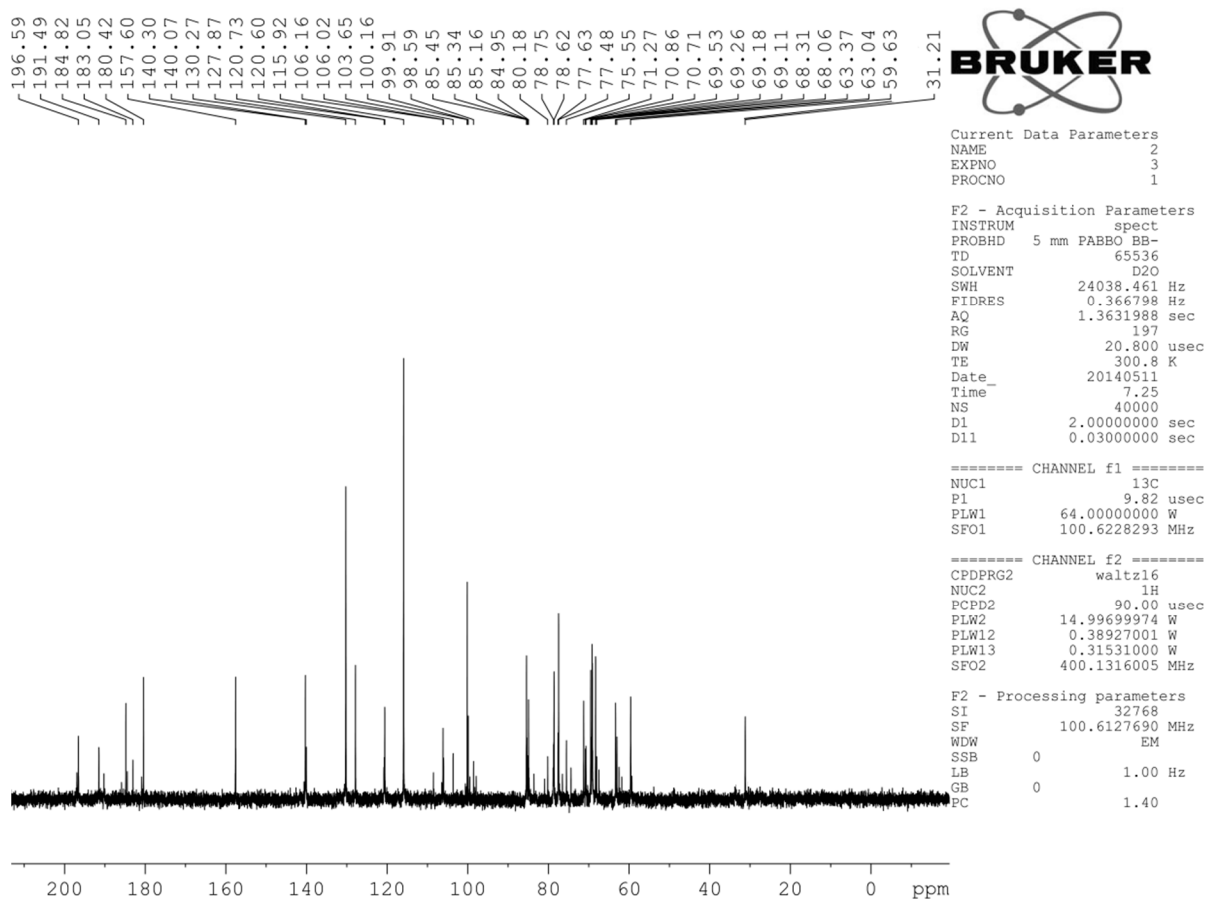
Figure S13. $^1\text{H-NMR}$ spectrum of hydroxysafflor yellow C (2) in D_2O .Figure S14. $^{13}\text{C-NMR}$ spectrum of hydroxysafflor yellow C (2) in D_2O .

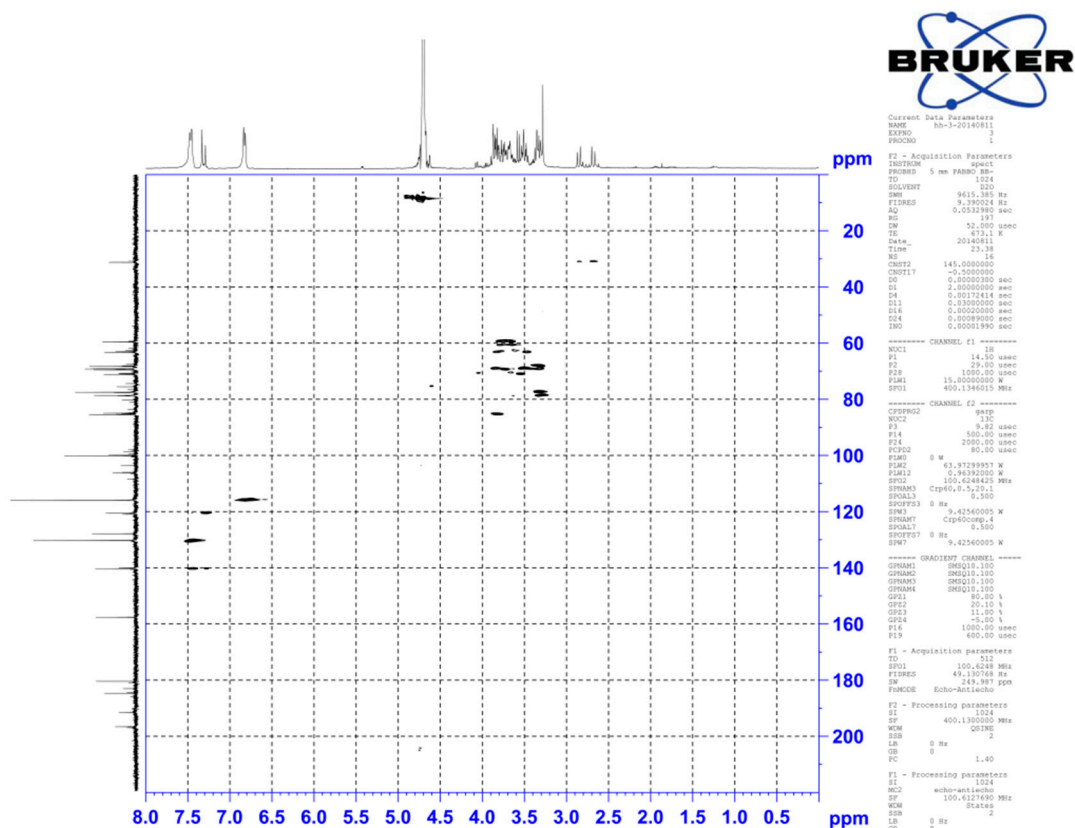
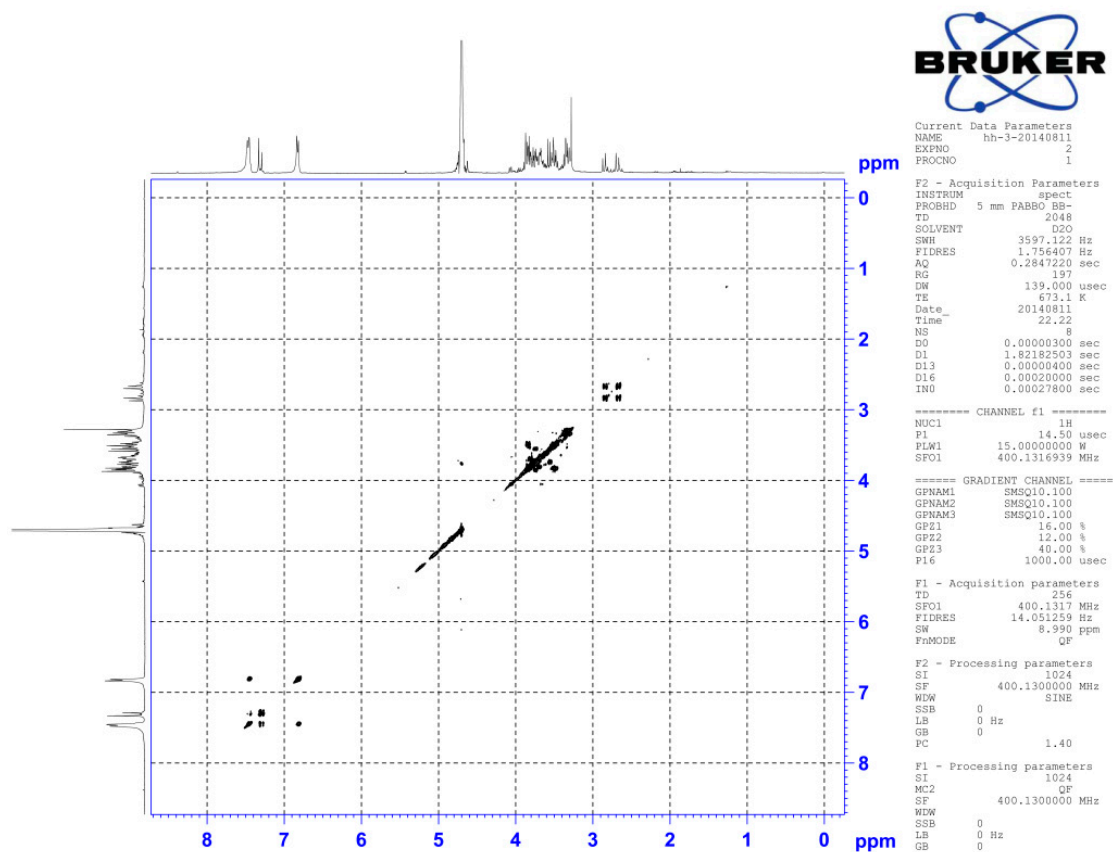
Figure S15. HSQC NMR spectrum of hydroxysafflor yellow C (2) in D₂O.Figure S16. COSY NMR spectrum of hydroxysafflor yellow C (2) in D₂O.

Figure S17. ^1H NMR spectrum of saffloquinoside C (4) in D_2O .