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ASSIGNMENT OF THE ^{13}C NMR SPECTRUM OF QUINOVIC ACID

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Key Word Index—^{13}C NMR spectra; triterpenes; quinovic acid; methyl quinovate; azizic acid; manevalic acid.

Abstract—The ^{13}C NMR spectra of the triterpene quinovic acid and its methyl ester have been assigned. The structures of azizic and manevalic acids should be revised.

The ^{13}C NMR spectra of triterpene acids of the urs-12-ene (ursolic acid, **1**) and olean-12-ene (oleanolic acid, **2**) types have been well documented. Doddrell *et al.* [1] reported the stereochemical dependence of ^{13}C chemical shifts in the two series, and assigned chemical shifts for C-12, C-13 and for hydroxylated carbons. They found that ^{13}C NMR spectroscopy is the most precise tool for the purpose of distinguishing between the two types, which is not easy otherwise. Tori and co-workers [2, 3] gave complete assignments of the ^{13}C signals of several urs-12-enes and olean-12-enes.

^{13}C NMR spectra can be used to distinguish between the two types by observing the chemical shift of C-12 and particularly that of C-13. In general, C-12 is deshielded (-2 ppm) and C-13 shielded (-5 ppm) in the urs-12-ene series and appears at 140 ppm, whereas the latter resonates at 144–145 ppm in the olean-12-ene series. The difference between the two values has been rationalized by the presence of a 19β (equatorial) methyl group which is in close proximity to the double bond (γ and γ' to C-13 and C-12, respectively) in the urs-12-ene series, thus effecting sterically the chemical shifts of these carbons. Introduction of a 19α-(axial)hydroxyl group was found to have a minor effect on the chemical shifts of C-12 and C-13, but the 19β-hydroxyl group has the same effect as the methyl group. The presence of a carboxyl group at C-14 (γ and γ' to C-13 and C-12, respectively) has a marked effect on the chemical shift. Thus the chemical shifts of C-12 and C-13 in **3** in the urs-12-ene series are at 128.5 and 133.5 ppm, respectively [1], while they are close to 126 and 137 ppm for **4**, **5** and **6** in the olean-12-ene series [4].

We report herein the ^{13}C NMR spectra of quinovic acid (**7**) and dimethyl quinovate (**8**); this is the first report giving the complete assignment of a triterpene acid of the ursolic type bearing a COOH at C-14. Assignment of the carbon chemical shifts in the ^{13}C NMR spectra was made by the use of the single frequency off-resonance decoupling technique [5, 6], application of known chemical shift rules due to hydroxyl and acetoxyl substituent groups, and steric effects [1, 5, 7, 8], as well as by comparison with the ^{13}C NMR spectral data of known ursene and oleanene derivatives [9, 10]. The chemical shifts of **7** (Table 1), especially those of C-12 and C-13, which resonate at 128.6 and 133.7 ppm, respectively, clearly corroborate the results and conclusions of Doddrell *et al.* [1].

Table 1. ^{13}C NMR chemical shifts of compounds **7** and **8**

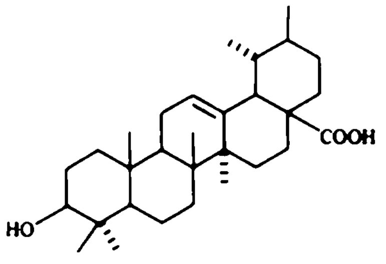
Carbon No.	**7**	**8**	Carbon No.	**7**	**8**
1	39.02	38.60	16	25.24	24.65
2	26.06	25.13	17	47.02	48.49
3	77.80	78.70	18	54.60	53.72
4	39.02	38.74	19	37.10	36.90
5	55.48	56.12	20	37.20	36.90
6	18.72	18.25	21	30.35	29.80
7	36.87	32.00	22	36.87	35.98
8	39.71	39. 7	23	27.82	27.18
9	48.43	47.30	24	16.08	16.30
10	37.20	37.05	25	16.40	16.30
11	23.13	22.77	26	18.02	15.60
12	128.60	129.28	27	177.70	175.40
13	133.70	131.98	28	179.88	177.80
14	56.47	51.48	29	18.72	17.00
15	28.80	28.06	30	21.19	21.00
			COOMe		51.10, 51.40

Application of these results to azizic acid (**9**) and manevalic acid (**10**) [11] (Table 2) clearly shows that the carboxyl group cannot be present at C-14 because the

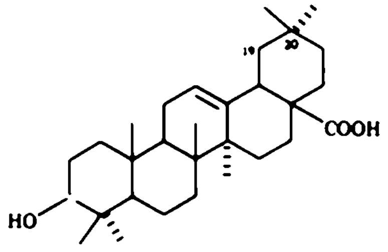
Table 2. Some ^{13}C NMR spectral data of compounds **4**–**6** and **9**–**13**

Compound	C-12	C-13
4	126.0	137.6
5	126.8	136.1
6	125.5	137.5
9	123.0	143.1
10	122.3	143.8
11*	125.1	138.0
12†	122.8	144.7
13‡	122.8	142.8

*Data taken from ref. [12].
†Data taken from ref. [13].
‡Data taken from ref. [14].



1



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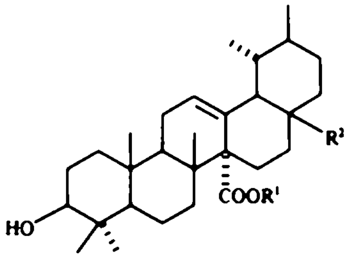
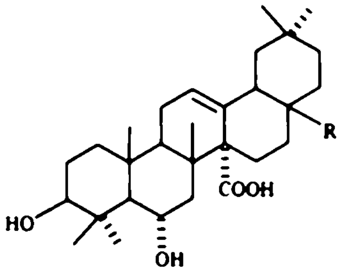
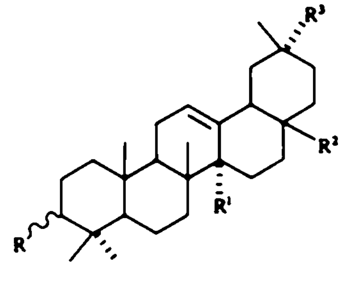


	R¹	R²
3	Me	CH_2OH
7	H	COOH
8	Me	COOMe



	R
9	COOH
10	Me



	R	R¹	R²	R³
4	α-OH	COOH	Me	Me
5	α-OH	COOH	Me	CHO
6	α-OH	COOH	Me	COOH
11	β-OH	Me	COOMe	Me
2	α-OAc	Me	Me	COOMe
13	β-OH	Me	COOMe	COOMe

chemical shifts of C-12 and C-13 in both **9** and **10** have normal values of the oleanolic acid type as in **11–13** (Table 2) and show no shielding effect of a carboxyl group. In view of this finding, we believe that the structures of **9** and **10** should be revised.

EXPERIMENTAL

Quinovic acid was isolated from *Fagonia cretica* as described earlier in ref. [15], and its dimethyl ester was prepared in the same way. Quinovic acid was fully characterized by spectroscopic techniques by comparing the ^{1}H NMR and mass spectra with those described recently in the literature [16].

The ^{13}C NMR spectra were obtained in $CDCl_3$ (pyridine-d_5) for quinovic acid at 25 MHz with TMS as internal standard.

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