Chemistry of the Annonaceae, Part 29.[1] Structure of Mezzettiaside-2, -4, -5, -6 and -7, New Partially Esterified 1-*O*-Octyl Tri- and Tetra-rhamnosyl Derivatives from *Mezzettia leptopoda*

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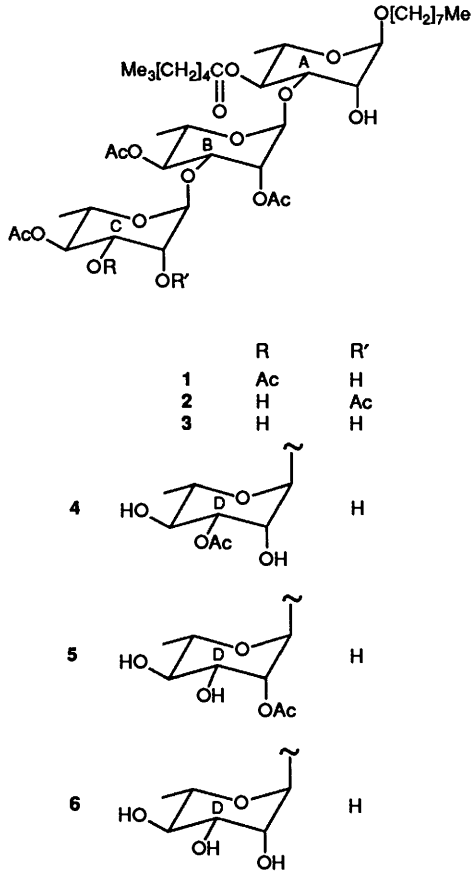
Extensive NMR and MS studies have led to the characterization of mezzettiasides-2, -4, -5, -6 and -7 from the stem bark of *Mezzettia leptopoda* (Annonaceae). All mezzettiasides isolated to date are based on an octyl 4-*O*-acetyl-α-L-rhamnopyranosyl-(1 ⟶ 3)-2,4-di-*O*-acetyl-α-L-rhamnopyranosyl-(1 ⟶ 3)-4-*O*-hexanoyl-α-L-rhamnopyranoside nucleus (= mezzettiaside-4). Mezzettiaside-2 has an additional *O*-acetyl substituent at C-2 of the terminal hexose and mezzettiasides-5 to -7 an additional 1 ⟶ 3-linked α-L-rhamnose unit at C-3 of that hexose (=mezzettiaside-7). Mezzettiaside-5 has C-3 of the additional hexose unit *O*-acetylated; in mezzettiaside-6 C-2 of that unit is *O*-acetylated

Recently, a number of unusual oligosaccharide derivatives have been obtained from bark extracts of species of Annonaceae originating from both Africa and Southeast Asia. The first of these to be fully characterised, reported from the African species *Cleistopholis glauca*,[2] were a series of tri- and tetra-α-L-rhamnosides characterised by a dodecyl ether (the genin) linked to C-1 of an α-L-rhamnose unit. Individual compounds differed in whether interglycosidic links were 1 ⟶ 3 or 1 ⟶ 4 and in the number and positions of acetoxy substituents on the rhamnose units. Concurrently, studies on the Malaysian species *Mezzettia leptopoda* Oliv. *ex* King yielded six allied oligosaccharides, partial structures for which were proposed by Etse.[3] Recently, one of these compounds, mezzettiaside-3, has been characterised as octyl 3,4-*di*-*O*-acetyl-α-L-rhamnopyranosyl-(1 ⟶ 3)-2,4-di-*O*-acetyl-α-L-rhamnopyranosyl-(1 ⟶ 3)-4-*O*-hexanoyl-α-L-rhamnopyranoside **1** as a result of extensive spectroscopic studies.[4]

In this paper we report the characterisation of five further mezzettiasides as octyl 2,4-di-*O*-acetyl-α-L-rhamnopyranosyl-(1 ⟶ 3)-2,4-di-*O*-acetyl-α-L-rhamnopyranosyl-(1 ⟶ 3)-4-*O*-hexanoyl-α-L-rhamnopyranoside (mezzettiaside-2, **2**), octyl 4-*O*-acetyl-α-L-rhamnopyranosyl-(1 ⟶ 3)-2,4-di-*O*-acetyl-α-L-rhamnopyranosyl-(1 ⟶ 3)-4-*O*-hexanoyl-α-L-rhamnopyranoside (mezzettiaside-4, **3**), octyl 3-*O*-acetyl-α-L-rhamnopyranosyl-(1 ⟶ 3)-4-*O*-acetyl-α-L-rhamnopyranosyl-(1 ⟶ 3)-2,4-di-*O*-acetyl-α-L-rhamnopyranosyl-(1 ⟶ 3)-4-*O*-hexanoyl-α-L-rhamnopyranoside (mezzettiaside-5, **4**), octyl 2-*O*-acetyl-α-L-rhamnopyranosyl-(1 ⟶ 3)-4-*O*-acetyl-α-L-rhamnopyranosyl-(1 ⟶ 3)-2,4-di-*O*-acetyl-α-L-rhamnopyranosyl-(1 ⟶ 3)-4-*O*-hexanoyl-α-L-rhamnopyranoside (mezzettiaside-6, **5**), and octyl rhamnopyranosyl-(1 ⟶ 3)-4-*O*-acetyl-α-L-rhamnopyranosyl-(1 ⟶ 3)-2,4-di-*O*-acetyl-α-L-rhamnopyranosyl-(1 ⟶ 3)-4-*O*-hexanoyl-α-L-rhamnopyranoside (mezzettiaside-7, **6**).



	R	R'
1	Ac	H
2	H	Ac
3	H	H
4		H
5		H
6		H

Results and Discussion

The six mezzettiasides were extracted from the stem bark of *Mezzettia leptopoda* with light petroleum (b.p. range 40–60 °C) and were purified by column chromatography and subsequent preparative centrifugal TLC. These were named mezzettiasides 2–7, based on the order of their elution from a silica gel column using a solvent mixture of toluene containing increasing amounts of ethyl acetate. All purified compounds were gums exhibiting negative specific rotation ($[\alpha]_D$ −31° to −63°).

Determination of Gross Structure.—The ^{1}H NMR spectra of all six compounds showed the following common features: (i) signals attributable to 1-H to 6-H of either three (**1**–**3**) or four (**4**–**6**) rhamnopyranose moieties were identifed by analysis of 2D homonuclear chemical-shift correlation (COSY) and relayed

Table 1 ^{1}H NMR chemical-shift data for compounds **2**–**6**; all spectra were run in CD_3OD–C_6D_6 (*ca.* 6:1) with δ-values quoted relative to δ 7.44 for the C_6H_6 resonance.

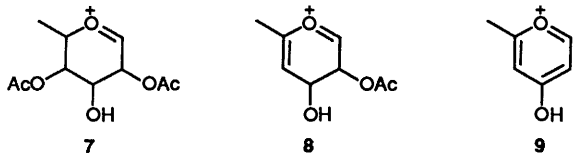
	2	**3**	**4**	**5**	**6**
A-1	5.08 d	5.13	5.18	5.11	5.15
A-2	4.35 dd	4.40	4.40	4.40	4.41
A-3	4.33 dd	4.38	4.37	4.40	4.42
A-4	5.65 dd	5.67	5.71	5.68	5.71
A-5	4.16 dq	4.17	4.19	4.17	4.18
A-6	1.49 d	1.51	1.51	1.51	1.53
B-1	5.16	5.21	5.24	5.21	5.23
B-2	5.50	5.53	5.59	5.56	5.58
B-3	4.72	4.75	4.79	4.75	4.79
B-4	5.56	5.59	5.64	5.61	5.64
B-5	4.49	4.49	4.51	4.50	4.50
B-6	1.45	1.47	1.47	1.46	1.48
C-1	5.28	5.38	5.42	5.34	5.40
C-2	5.38	4.27	4.40	4.30	4.38
C-3	4.38	4.26	4.41	4.32	4.37
C-4	5.42	5.44	5.65	5.60	5.59
C-5	4.23	4.23	4.27	4.25	4.28
C-6	1.57	1.57	1.55	1.54	1.56
D-1			5.32	5.25	5.33
D-2			4.42	5.41	4.27
D-3			5.55	4.42	4.27
D-4			4.14	3.91	3.95
D-5			4.40	4.25	4.28
D-6			1.80	1.73	1.78
Ac	2.30 (C-2)	2.18 (B-4)	2.24 (C-4)	2.27 (C-4)	2.24 (C-4)
	2.11	2.06 (C-4)	2.23 (D-3)	2.18 (B-4)	2.08 (B-4)
	2.08	1.96 (B-2)	2.09 (B-4)	2.07 (D-2)	2.00 (B-2)
	2.01 (B-2)		2.00 (B-2)	2.00 (B-2)	
$COCH_2$[a]	2.75/2.57	2.78/2.57	2.77/2.60	2.78/2.57	2.79/2.57
OCH_2[b]	3.84/3.53	3.84/3.53	3.84/3.51	3.84/3.50	3.82/3.50
Me[c]	1.09/1.07	1.09/1.06	1.10/1.07	1.09/1.07	1.09/1.06

Coupling constants: hexose systems, **1**–**2** 1.0–2.02 Hz, **2**–**3** 3.0–3.5 Hz, **3**–**4** 9.7–9.9 Hz, **4**–**5** 9.8–9.9 Hz, **5**–**6** 6.1–6.4 Hz. [a] Each resonance is a dt (16.1, 7.7 Hz). [b] Each resonance is a dt (9.7, 6.7 Hz). [c] t with *J* 6.5–7.0 Hz.

COSY experiments; (ii) methylene resonances assignable to $-COCH_2-$ and $-OCH_2-$ moieties, which could be extrapolated to $COCH_2[CH_2]_nMe$ and $OCH_2[CH_2]_nMe$ substituents; (iii) signals assignable to either three (**3**, **6**) or four (**1**, **2**, **4**, **5**) *o*-acetyl substituents.

MS data on mezzettiasides have been obtained using several different techniques. As already reported,[4] negative-ion FAB-MS was successful in giving a weak $[M - H]^-$ ion for compound **1** (*m/z* 833; M 834, $C_{40}H_{66}O_{18}$). Likewise, positive-ion FAB-MS yielded a weak $[M + Na]^+$ ion at *m/z* 815 for compound **3**, so indicating a molecular weight of 792 ($C_{38}H_{64}O_{17}$), 42 daltons (one acetyl substituent) less than that for compound **1**. For compound **6** californium plasma desorption (CPD)–MS[5] revealed a strong pseudomolecular ion at *m/z* 960 which can be attributed to $[M - H + Na]^+$ which, given three acetate substituents together with the same alkanoate and alkyl ether as in compound **3**, solves for four rhamnose units (M 938, $C_{44}H_{74}O_{21}$). Direct probe CI-MS gave a highest *m/z* 793 for compounds **3**–**6** and one at *m/z* 835 for compounds **1** and **2**. This ion represents $[M + 1]^+$ in the trirhamnosides but in the tetrarhamnosides requires a readily occurring loss of one hexose unit to leave a fragment with composition identical with compound **3**. EI-MS was not very useful; in each compound the base peak was *m/z* 43 (acetate), with other major ions at *m/z* 231 (**7**, $C_{10}H_{15}O_6$), 171 (**8**, $C_8H_{11}O_4$) and 111 (**9**, $C_6H_7O_2$) representing a single pyran ring in various stages of deesterification and dehydration.

Substitution Patterns on Hexose Units.—Patterns of substitution on individual hexose units were studied primarily by ^{1}H NMR spectroscopy. 1D Spectra were initially obtained in



7 **8** **9**

$CDCl_3$ but these were difficult to interpret due to signal bunching. Signal dispersion was greatly improved by using a solvent made up of CD_3OD and C_6D_6 in the ratio of ~6:1. Use of this solvent and a range of 2D homonuclear techniques (COSY, COSY-45, relayed COSY) made it possible to assign chemical-shift values for all C-bonded protons in each hexose moiety (Table 1). ^{13}C NMR spectra were also obtained for each compound and signals were assigned by 2D HMQC (Heteronuclear Multiple Quantum Coherence) studies in the same solvent mixture (Table 2). The assignment of series of signals to individual rings (rings A, B, C and, in compounds **4**–**6**, D) is discussed below.

From the ^{1}H NMR spectra, esterified positions on hexose units were easily identified through strong deshielding effects. Thus, in all compounds, positions A-4, B-2, B-4 and C-4 were obviously substituted. An additional esterification must occur at C-2 in compound **2**, D-2 in compound **5** and D-3 in compound **4**. In each compound one esterifying group must be the alkanoate and the remaining three or four are acetyl.

Location of Interglycosidic Links and Position of Ether and Ester Substituents.—These were established almost entirely on the basis of detailed long-range (^2J, ^3J) heteronuclear coupling [correlation *via* large-range coupling (COLOC), (HMBC)-(Heteronuclear Multiple Bond Coherence)] studies. These

Table 2 ^{13}C NMR chemical-shift data for compounds **2**–**6**. Letters in parentheses in the same column indicate interchangeable signals. Spectra run in $CDCl_3$

	2	3	4	5	6
A-1	100.6	100.8	100.5	100.5	100.7
A-2	71.5	71.9	69.5	71.5	71.8
A-3	79.2	79.4	79.0	79.0	79.1
A-4	72.8	73.1	72.8	72.7	73.2
A-5	67.1	67.4	67.1	67.1	67.3
A-6	17.6	17.9	17.8[a]	17.6	17.9
B-1	100.2	100.4	100.0	100.0	100.2
B-2	72.5	72.8	72.5	72.4	72.6
B-3	75.4	75.4	75.7	75.6	75.9
B-4	73.1	73.6	73.0	73.0	73.2
B-5	67.6	67.9	67.5	67.5	67.7
B-6	17.3	17.8	17.7[a]	17.6	17.6
C-1	100.0	103.1	102.6	102.6	102.9
C-2	73.4	72.0	71.6[b]	71.5	71.6
C-3	67.7	70.3	76.7	77.3	77.1
C-4	74.5	75.1	73.3	73.0	73.6
C-5	67.7	67.9	68.0	68.0	68.1
C-6	17.3	17.6	17.4	17.4	17.6
D-1			102.3	100.2	103.0
D-2			71.3[b]	73.3	71.8
D-3			74.9	69.5	71.8
D-4			70.8	73.4	73.5
D-5			70.0	69.5	69.7
D-6			17.4	17.4	17.9
CO*Me*	20.4 (C-2)	20.9 (B-4)	20.7	20.6 (C-4)	20.7 (C-4)
	20.3	20.7 (C-4)	20.5	20.4 (B-4)	20.6 (B-4)
	20.2	20.4 (B-2)	20.4 (B-4)	20.4 (D-2)	20.5 (B-2)
	20.1 (B-2)		20.3 (B-2)	20.3 (B-2)	
*C*OMe	171.5 (C-2)	171.8 (C-4)	171.9 (D-3)	171.3 (C-4)	170.9 (C-4)
	171.5 (B-2)	170.9 (B-4)	170.8 (B-4)	171.1 (D-2)	170.6 (B-4)
	171.2	170.8 (B-2)	170.6 (C-4)	170.6 (B-2)	170.6 (B-2)
	171.1		170.5 (B-2)	170.4 (B-4)	
CO	173.6	173.9	173.7	173.7	173.9
CH_2	34.4	34.8	34.4	34.4	34.6
CH_2	24.9	25.2	24.9	24.9	25.1
CH_2	31.6	31.9	31.6	31.6	31.8
CH_2	22.6	22.9	22.6	22.6	22.8
Me	14.0[a]	14.2[a]	14.0[c]	13.9[a]	14.2[a]
OCH_2	68.2	68.3	68.2	68.2	68.4
CH_2	29.8	30.1	29.7	29.8	30.0
CH_2	26.5	26.8	26.5	26.5	26.8
CH_2CH_2	29.5/29.6	29.9/29.8	29.8/29.5	29.7/29.6	29.8/29.7
CH_2	32.1	32.4	32.1	32.1	32.3
CH_2	22.9	23.2	23.0	23.0	23.6
Me	14.2[a]	14.4[a]	14.2[c]	14.1[a]	14.4[a]

experiments were run in the same mixed solvent, optimized for 5.5–7 Hz coupling constants, and with pulse delays varying between 70 and 90 ms. It was generally necessary to perform the experiment with different delay times in order to obtain all the important connectivities for a given compound when using COLOC but where HMBC was employed all relevant data was obtained in a single experiment. The following features were common to all compounds:

(i) A ^3J-interaction between the alkoxy methylene carbon (δ_C 68.2–68.4) and an anomeric proton of one of the rhamnose units. This 1-*O*-alkyl ether can be considered to be the 'genin' and assigned to the rhamnose unit designated as 'A' (see Tables 1 and 2).

(ii) A series of ^3J-interactions between 3-H or C-3 of one rhamnose unit and C-1 or 1-H of another. This established a consistent 3 ⟶ 1 linkage between the hexoses. These were then numbered accordingly; *e.g.* A ⟶ B ⟶ C (⟶ D).

(iii) The most deshielded carbonyl resonance (δ_C 173.9–173.6) can be assigned to the alkanoate (^2J-coupling with methylene protons δ_H *ca.* 2.5–2.8 on the adjacent carbon). In each compound this substituent could be placed at A-4 as the carbonyl also exhibited ^3J-coupling to 4-H (δ_H *ca.* 5.7) in the A-ring.

The remaining esterified positions are, therefore, acetylated. Through HMBC experiments it was possible, in most cases, to link specific acetyl carbonyls with their corresponding ^1H methyl resonances (^2J) and the ring proton at the position of esterification (^3J).

Identification of A-1 *and* A-4 *Substituents.*—In compound **1** the occurrence of an octyl ether and *O*-hexanoyl moieties was established from FAB-MS, and their sites of substitution by NMR spectroscopy. In the present study the use of HMBC analysis alone proved to be sufficient to identify the carbon resonances of the hexanoyl unit using the following strategy:

(i) ^3J-interactions were visible between the deshielded 2-H protons and C-4 (δ_C 31.9–31.6).

(ii) C-4 Always showed a further ^3J-coupling with the protons of one of the methyl groups, thus terminating the chain at six carbons.

Configuration of Rhamnose at C-1.— As 2-H of rhamnose is equatorial it is not possible to distinguish between α-rhamnose (1-H equatorial) and β-rhamnose (1-H axial) by J_{H1-2} which is, in both cases, of the order of 1–2 Hz. One reliable manner of distinguishing between α- and β-rhamnose is through J_{C-H} for

C-1/1-H. A series of gated decoupling studies was undertaken and results are exemplified by those for compound **5** which showed J_{C1-H1}-values 168.6 Hz for A-1, 168.2 Hz for B-1, 166.0 Hz for C-1 and 167.4 Hz for D-1. This is typical of the α-configuration.[6,7] Further evidence for the equatorial (α) configuration of the anomeric proton came from the observation of long-range (^5J) coupling between 1-H and 6-H in delayed COSY experiments. This coupling is due to an extended zig-zag pathway 1-H and the 6-H (methyl) protons.[8] We concluded that all the studied compounds were based on α-rhamnose.

Absolute Configuration of Rhamnose Units.—The stereochemistry of the hexose units in compound **1** was assigned as α-L-rhamnose.[4] In view of the comparable specific rotation found in compounds **2**–**6** we concluded that these were also made up of α-L-rhamnose monomers.

Other oligosaccharides with some similarity to those found in the Annonaceae (1 ⟶ 2- and 1 ⟶ 3-linked tetrarhamnosides) have recently been isolated from *Calonyction aculeatum*[9] and are reported to act as plant-growth substances. Studies on the bioactivity of the mezzettiasides are in progress.

Experimental

NMR experiments were conducted on a Bruker AC300 instrument which was modified in order to allow detection in the reverse mode. COSY, delayed COSY, COLOC, HMQC and HMBC experiments were performed using the Bruker library of microprograms. For the homonuclear experiments, matrices were 256 × 1K data points and, for the heteronuclear, 256 × 2K data points. Sine bell multiplication was applied in both dimensions before Fourier transformation, except for HMBC and HMQC experiments where a shift of 60° was applied.

Plant Material.—Stem bark of *Mezzettia leptopoda* was collected in the Krau Game Reserve, West Malaysia.

Extraction of Stem Bark. Ground bark (250 g) was extracted (Soxhlet) with light petroleum (b.p. range 40–60 °C). The concentrated extract was subjected to column chromatography over silica gel and eluted with toluene and then toluene containing increasing amounts of ethyl acetate. Thus yielded five bands as follows: 10% ethyl acetate gave crude compound **2**; 15%, crude compound **1**; 20%, crude compound **3**; 30%, a mixture of isomers **4** and **5**; 40%, crude compound **6**. Each fraction was then purified by preparative centrifugal TLC with chloroform–methanol mixtures as developer. Thus development of crude **2** from the plates with chloroform–methanol (99:1) yielded pure compound **2** (100 mg). Likewise, development with chloroform–methanol (19:1) gave compound **1** (250 mg); (92:8) gave compound **3** (200 mg); (9:1) gave compound **4** (50 mg); and (88:12) gave compound **5** (30 mg). Finally development with the ratio 86:15 yielded compound **6** (220 mg).

Mezzettiaside-2 **2**.—Gum, $[\alpha]_D$ −31° (*c* 0.25, $CHCl_3$); ν_{max}(film)/cm^{-1} 3500, 2940, 2850, 1740, 1380 and 1240; for ^{1}H and ^{13}C NMR data, see Tables 1 and 2, respectively; *m/z* (CI-MS, probe) 793 ($C_{38}H_{64}O_{17}$ + H); (EI-MS) 231 ($C_{10}H_{15}O_6$, 100%), 171 ($C_8H_{11}O_4$, 62), 153 ($C_8H_9O_3$, 44), 111 ($C_6H_7O_2$, 55) and 43 (C_2H_3O, 91).

Mezzettiaside-4 **3**.—Gum, $[\alpha]_D$ −54° (*c* 0.46, $CHCl_3$); ν_{max}(film)/cm^{-1} 3500, 2940, 2850, 1740, 1380 and 1240; for ^{1}H and ^{13}C NMR data, see Tables 1 and 2, respectively; *m/z* (FAB-MS) 815 (M^+, 792 + Na, $C_{38}H_{64}O_{17}$); (CI-MS, probe) 793 ($C_{38}H_{64}O_{17}$ + H); (EI-MS) 231 ($C_{10}H_{15}O_6$, 88%), 213 ($C_{10}H_{13}O_5$, 32) 189 ($C_{38}H_{13}O_5$, 85), 171 ($C_8H_{11}O_4$, 73), 153 ($C_8H_9O_3$, 61), 129 ($C_6H_9O_2$, 43) 111 ($C_6H_7O_2$, 72) and 43 (C_2H_3O, 100).

Mezzettiaside-5 **4**.—Gum, $[\alpha]_D$ −57° (*c* 0.37, $CHCl_3$); ν_{max}(film)/cm^{-1} 3500, 2940, 2850, 1740, 1380 and 1240; for ^{1}H and ^{13}C NMR data, see Tables 1 and 2, respectively; *m/z* (CI-MS, probe) 835 ($C_{40}H_{67}O_{18}$ + H); (EI-MS) 231 ($C_{10}H_{15}O_6$, 40%), 171 ($C_8H_{11}O_4$, 64), 111 ($C_6H_7O_2$, 70) and 43 (C_2H_3O, 100).

Mezzettiaside-6 **5**.—Gum, $[\alpha]_D$ −35° (*c* 0.23, $CHCl_3$); ν_{max}(film)/cm^{-1} 3500, 2940, 2850, 1740, 1380 and 1240; for ^{1}H NMR data, see Table 1; *m/z* (CI-MS, probe) 835 ($C_{40}H_{67}O_{18}$ + H); (EI-MS) 231 ($C_{10}H_{15}O_6$, 57%), 189 ($C_8H_{13}O_5$, 46), 171 ($C_8H_{11}O_4$, 55), 111 ($C_{36}H_7O_2$, 55) and 43 (C_2H_3O, 100).

Mezzettiaside-7 **6**.—Gum, $[\alpha]_D$ −63° (*c* 0.54, $CHCl_3$); ν_{max}(film)/cm^{-1} 3500, 2940, 2850, 1740, 1380 and 1240; for ^{1}H and ^{13}C NMR data, see Tables 1 and 2, respectively; *m/z* (CPD-MS) 960 (M − H + Na, $C_{44}H_{74}O_{21}$); (CI-MS, probe) 793 ($C_{38}H_{64}O_{17}$ + H); (EI-MS) 231 ($C_{10}H_{15}O_6$, 88%), 213 ($C_{10}H_{13}O_5$, 32), 189 ($C_8H_{13}O_5$, 85), 171 ($C_8H_{11}O_4$, 73), 153 ($C_8H_9O_3$, 61), 129 ($C_6H_9O_2$, 43), 111 ($C_6H_7O_2$, 72) and 43 (C_2H_3O, 100).

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