# $^{13}C$ NMR SPECTROSCOPY OF OLEANANE DERIVATIVES

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The chemical shifts of the carbon atoms in the $^{13}C$ NMR spectrum of 188 natural and synthetic oleanane derivatives published up to 1988 are given. The possibilities of $^{13}C$ NMR spectroscopy for the identification and study of the structures of new derivatives are discussed.

Information on $^{13}C$ NMR spectra of triterpenoids up to 1976 was given in Wehrli and Nishida's review [1]. This review contains nine references to publications devoted to the spectra of triterpenoids. Since that time, the use of $^{13}C$ NMR spectroscopy has, in the overwhelming majority of cases, become an integral part of the procedure for establishing the structure of new triterpenoids. Furthermore, the recording of the spectra of the triterpenoids of already established structure permits their more complete characterization for the purpose of their subsequent identification.

Some of the most widespread natural triterpenoids are triterpenoids of the oleanane series. The spectra of oleanolic acid and its 3-oxo derivatives, hederagenin, queretaroic acid, gypsogenin, quillaic acid, 22α-hydroxyerythrodiol, 23-hydroxyerythrodiol, the methyl esters of maslinic and 3-epimaslinic acids, β-amyrin, 16-deoxysaikogenin G, deoxysaikogenin G, deoxysaikogenin E, deoxysaikogenin F, 22α-hydroxysaikogenin, 23-hydroxyprimulagenin, longispinogenin, and 23-hydroxyllongispinogenin were given and discussed in [1]. The corresponding spectra were given in Tables 1-24. The procedure of assigning the signals in the spectra of these compounds, together with the effects of available substituents, were discussed in the paper cited. In subsequent publications, the assignment of the signals in the spectra of oleanane derivatives was made on the basis of the spectra of the above-mentioned compounds and, as a rule, was not described. In the general case, the $^{13}C$ NMR spectrum taken in the regime of complete decoupling from protons consists of a set of singlet signals characterized by their CS values and, after the application of specially experimental procedures [6], a statement of the type of carbon atoms (C, CH, $CH_2$, $CH_3$) to which a given signal belongs. The method of assigning the signals in such spectra of polycyclic natural compounds has been described in detail in the literature [1-6]. In this review, we have attempted to consider the $^{13}C$ NMR spectra of oleanane triterpenoids published up to and including 1988, with some from 1989. Since triterpenoids are frequently present as the aglycons in glycosides, in Tables 25 and 26 we give values of the glycosylation shifts obtained on the substitution of a hydroxy group of a sugar residue. The spectra of the glycosides are usually obtained by dissolving them in pyridine. Therefore, in those cases where the spectrum of the aglycon was taken in chloroform, these values bear an arbitrary nature to a considerable degree, because of the influence of the solvent on the SCs. Thus, the signals of carbon atoms attached to a hydroxy group adjacent to it have a downfield shift, in comparison with the spectra taken in chloroform, reaching 2-3 ppm [30]. Furthermore, the values of the glycosylation shifts for one and the same aglycon depend on the type of carbohydrate chain.

Solvation shifts are shown in partial formulas 4b and 98a.

The changes in the CSs of the carbon atoms on the introduction of methoxycarbonyl group into the C-17 position of β-amyrin (1) and of a hydroxy group into the C-23 and C-24 positions of oleanolic acid (2) are shown in the partial formulas 2a, 4a, and 6a, respectively. The structure of 4-epihederagenin (6) was established mainly by chemical methods [8]. Nevertheless, the difference between its $^{13}C$ NMR spectrum and that of hederagenin (3) is readily explained on the basis of the effects of the substituents at C-24 and C-23 on their CSs [5]. As can be seen from the Tables of CSs given, these differences are most pronounced for the CSs of the carbon atoms C-5 (+6.8 ppm) and C-3 (+3.9 ppm). Also characteristic is the up-

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TABLE 1. $^{13}C$ NMR Spectra of Compounds (1)-(8)*

| C | $1^{C}$ | $2^{C}$ | $3^{C}$ | $4^{C}$ | $5^{C}$ | $6^{P}$ | $7^{C}$ | $8^{P}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 38,5 | 38,5 | 39.1 | 38,1 | 38,8 | 38,8 | 38.7 | 33,9 |
| 2 | 27,0 | 27,1 | 34.2 | 26,4 | 35,2$^{a}$ | 28,5 | 34,4 | 26,4 |
| 3 | 78,9 | 78,7 | 216,8 | 76.4 | 219,0 | 80,3 | 217,6 | 70.0 |
| 4 | 38,7 | 38.7 | 47,3 | 41.7 | 49,3 | 43.3 | 51,3 | 43,8 |
| 5 | 55,1 | 55,2 | 55,2 | 49,7 | 52,4 | 56,5 | 55,9 | 50,1 |
| 6 | 18,3 | 18,3 | 19,5 | 18,5 | 19,2 | 19.1 | 19,3 | 19,1 |
| 7 | 32,6 | 32,6 | 32,1 | 32,4 | 32,3$^{b}$ | 33,6 | 32.4 | 33,6 |
| 8 | 39,7 | 39,3 | 39,1 | 39,3 | 39,3 | 39.8 | 39,2 | 39,9 |
| 9 | 47,6 | 47,6 | 46.7 | 47,5 | 46,8 | 48,3 | 46.6 | 48.1 |
| 10 | 37,0 | 37.0 | 36,6 | 36,9 | 36,6 | 37.3 | 36.6 | 37,5 |
| 11 | 23,4 | 23.1 | 23,0 | 23,1 | 23,5$^{c}$ | 24,1 | 23,1$^{b}$ | 24,0 |
| 12 | 121,7 | 122,1 | 121,9 | 122.2 | 122,0 | 122,7 | 122,1 | 122,9 |
| 13 | 145,0 | 143,4 | 143.5 | 143.6 | 144,1 | 145,1 | 143.9 | 144,1 |
| 14 | 41,7 | 41,6 | 41.7 | 41,7 | 41,8 | 42,2 | 41,5 | 42.0 |
| 15 | 28.3 | 27,7 | 27.6 | 27,7 | 27,7 | 28,5 | 27,7 | 28,1 |
| 16 | 26,2 | 23,4 | 23,5 | 23,4 | 23,1$^{c}$ | 23,8 | 23,8$^{b}$ | 23,5 |
| 17 | 32.5 | 46.6 | 46,7 | 46,7 | 46,7 | 46,8 | 46,8 | 47,0 |
| 18 | 47.2 | 41,3 | 41,2 | 41,3 | 41,4 | 42,1 | 41.5 | 41,9 |
| 19 | 46,8 | 45,8 | 45,7 | 45.9 | 45.8 | 46.6 | 45,9 | 46,2 |
| 20 | 31,1 | 30,6 | 30.5 | 30,7 | 30,7 | 31,0 | 30,7 | 30,8 |
| 21 | 34,8 | 33.8 | 33,7 | 33.9 | 33,9$^{a}$ | 34.3 | 33.9 | 34,0 |
| 22 | 37,2 | 32.3 | 32,1 | 32,4 | 32,1$^{b}$ | 33.3 | 32,1 | 32,8 |
| 23 | 28,1 | 28.1 | 26,4 | 71.3 | 67,0 | 23,7 | 22,0 | 23,4 |
| 24 | 15,5 | 15.6$^{a}$ | 21,3 | 11,6 | 17,0 | 64.6 | 65,8 | 65.8 |
| 25 | 15,5 | 15,3$^{a}$ | 14,8 | 15,7 | 15.2 | 16,0 | 16.0 | 15,9 |
| 26 | 16,8 | 16,8 | 16,7 | 16,9 | 16,8 | 17.3 | 16,6 | 17,1 |
| 27 | 26,0 | 26,0 | 25,7 | 26.0 | 25,9 | 26,2 | 25.8 | 26,1 |
| 28 | 27,3 | 177,9 | 177,7 | 178,2 | 178,2 | 180,4 | 178,3 | 177,9 |
| 29 | 33,2 | 33,1 | 33,0 | 33,1 | 33,1 | 33,3 | 33,1 | 33.1 |
| 30 | 23,6 | 23,6 | 23,5 | 23,6 | 23,6 | 23,8 | 23,6 | 23,7 |
| OMe |  | 51,3 | 51,3 | 51,6 |  |  |  | 51,7 |

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*Here and in the following tables, the letters C, P, D, and M indicate the type of solvent: chloroform-$d_1$, pyridine-$d_5$, dimethyl-$d_6$ sulfoxide, and methanol-$d_3$, respectively; the letters a, b, c, etc., above the values of the chemical shifts indicate an ambiguity of the assignment of the signals.

field shift (—4.4 ppm) of the C-23 signal (23.7 ppm) as compared with that of oleanolic acid in the spectrum of (6), while in the case of hederagenin it is the C-24 signal that undergoes a shift (11.6 ppm).

The epimerization of C-3 on passing from compound (6) to compound (8) causes characteristic changes in the C-1 CS (—4.5 ppm) and the C-5 CS (—6.4 ppm). $^{13}C$ NMR spectra were used by Ikuta and Itokawa [12] in estabishing the C-3 configuration of triterpenoids (11) and (12) isolated from a tissue culture of Akebia quinata.

The main difference between the spectra of (15) and (16), which are connected with the difference in the C-3 CSs, are due, on the one hand, to differences in the β-effects of the α- and β-OH groups at C-2 [58], and to the greater deviation from additivity of the CSs in the spectra of 1,2-diols for the case of cis-substitution [59], on the other hand. The effects of the replacement of a methyl group by an aldehyde group in gypsogenin (19) are shown in the partial formula (19a). As can be seen from the facts presented, the substitutions in ring A that have been mentioned are reflected appreciably only on the CSs of the carbon atoms of this ring. Exceptions are the C-1 substituted imberbic acid and its derivatives (72-75).

An analogous pattern is observed for the 18β-isomers of 11-oxooleanolic acid (20-22) [16]. The changes in the CSs of the carbon atoms of oleanolic acid on the introduction of an oxo group into position 11 are shown in partial formula 21a. Analysis of the figures in the tables shows a significant difference between the spectra of the 18β and 18α derivatives of 11-oxooleanolic acid (compounds 23-25) in the sections of the CSs of the C-12, C-13, C-16—C-19, C-22, and C-27—C-30 atoms. Partial formula 23a shows the changes in the CSs of the carbon atoms on passing from compounds (20-22) to (23-25). The isolation of the new triterpenoid (152) from Vellozia compacta has been described in [17]. The $^{13}C$ NMR spectrum of the product of its partial synthesis (26) confirms the proposed structure.

TABLE 2. $^{13}C$ NMR Spectra of Compounds (9)-(16)

| C | $9^{C}$ | $10^{C}$ | $11^{C}$ | $12^{C}$ | 13 | 14 | $15^{P}$ | $16^{P}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 33,1 | 33,6 | 38,5 | 33,0 | 41,4 | 38.5 | 47,6 | 44,9 |
| 2 | 25,3 | 22,6 | 27,2 | 25,2 | 66,2 | 67,7 | 68,8 | 71,6 |
| 3 | 70,8 | 73,5 | 79,2 | 76,2 | 73,3 | 72,4 | 78,2 | 73,0 |
| 4 | 41,3 | 40,6 | 38,8 | 37,4 | 41,4 | 41,6 | 43,6 | 42,3 |
| 5 | 49,6 | 50,9 | 55,2 | 49,0 | 48,5 | 50,1 | 48,0 | 48,5 |
| 6 | 18,6 | 18,4 | 18,3 | 18,3 | 18,2 | 18,0 | 18,5 | 18,3 |
| 7 | 33,0 | 33,0 | 32,7 | 32,7 | 32,7 | 32,5 | 32,9 | 33,2 |
| 8 | 39,6 | 39,6 | 39,4 | 39,5 | 39,3 | 39,3 | 39,8 | 39,9 |
| 9 | 47,7 | 47,7 | 47,7 | 47,5 | 47,4 | 47,5 | 48,1 | 48,1 |
| 10 | 37,0 | 36,9 | 37,1 | 37,1 | 37,9 | 38,1 | 38,4 | 37,2 |
| 11 | 23,6 | 23,6 | 23,3 | 23,3 | 23,3 | 23,5 | 23,7 | 24,0 |
| 12 | 122,4 | 122,3 | 123,2 | 123.0 | 121,9 | 121,8 | 123,2 | 122,7 |
| 13 | 143,9 | 143,8 | 143,1 | 143.2 | 143,7 | 143,8 | 144,9 | 144,8 |
| 14 | 41,8 | 41,8 | 41,6 | 41,8 | 41,6 | 42,0 | 44,2 | 42,4 |
| 15 | 27,8 | 27,8 | 27,7 | 27,7 | 27,5 | 27,5 | 28,3 | 28,3 |
| 16 | 23,2 | 23,2 | 23,5 | 23,4 | 22,9 | 22,9 | 23,9 | 23,8 |
| 17 | 46,8 | 46,8 | 47,0 | 47,1 | 46,6 | 46,5 | 47,6 | 46,6 |
| 18 | 41,5 | 41,5 | 41,4 | 41,4 | 41,1 | 41,1 | 42,0 | 42,0 |
| 19 | 46,1 | 46,1 | 47,2 | 47,2 | 45,7 | 45,8 | 46,4 | 46,4 |
| 20 | 30,7 | 30,7 | 148,0 | 148,2 | 30,6 | 30,6 | 30,9 | 30,9 |
| 21 | 34,0 | 34,0 | 30,0 | 30,0 | 33,7 | 33,7 | 34,1 | 34,2 |
| 22 | 32,5 | 32,5 | 37,5 | 37,5 | 32,2 | 32,2 | 33,2 | 33,0 |
| 23 | 22,3 | 22,0 | 28,1 | 28,3 | 22,0 | 22,1 | 66,6 | 67,6 |
| 24 | 67,8 | 66,8 | 15,6 | 22,3 | 65,5 | 66,1 | 14,2 | 14,5 |
| 25 | 15,6 | 15,6 | 15,3 | 15,3 | 16,6 | 16,6 | 17,3 | 17,3[a] |
| 26 | 16,8 | 16,8 | 16,8 | 16,9 | 16,6 | 16,6 | 17,5 | 17,5[a] |
| 27 | 26,1 | 26,0 | 26,0 | 26,2 | 25,9 | 25,9 | 26,1 | 26,2 |
| 28 | 178,2 | 178,1 | 177,5 | 177,5 | 178,2 | 178,1 | 180,0 | 180,2 |
| 29 | 33,1 | 33,1 | 106,8 | 107,0 | 33,0 | 33,0 | 33,2 | 33,2 |
| 30 | 23,7 | 23,7 |  |  | 23,5 | 23,5 | 23,7 | 23,8 |
| OMe | 51,4 | 51,4 | 51,6 | 51,6 | 51,4 | 51,5 |  |  |
| OAc | 171,0<br>20,8 | 171,0<br>170,3<br>20,8<br>21,2 |  |  |  | 171,1<br>170,3<br>170,1<br>21,1<br>20,9 |  |  |

The replacement of C-28 methyl group by a hydroxymethyl group (27) causes an upfield shift of the C-16, C-18, and C-22 signals and a downfield shift of the C-17 signal (27a).

The introduction of a hydroxy group into the C-30 position (30) causes an upfield shift of the signals of C-19 (—5.5 ppm), C-21 (—1.7 ppm), and C-29 (—4.2 ppm), and a downfield shift of the C-20 signal (+4.6 ppm) in comparison with methyl oleanolate. The difference between the spectra of compounds (29) and (30) amounts mainly to differences in the CSs of the substituted carbon atom (C-29 or C-30) and in the CSs of the methyl groups geminal to them [12] (see Tables 1 and 4). These results were used in establishing the C-20 configuration in compound (29) isolated from a tissue culture of the Akebia quinata. An analogous approach was used in establishing the C-20 configuration in the case of the 28,29-dihydroxy-olean-12-en-3-one from Orthosphenia mexicana [18]. The isolation of a new triterpenoid was described in [11], and its structure was confirmed by analysis of the $^{13}C$ NMR spectrum of its methyl ester (33). Serratagenic acid (34) was identified as the aglycon of glycosides from Nothopanax delavayi [19]. The changes in the screening of the carbon atoms of ring E on the introduction of a carboxy group into the C-20 position as compared with compounds (8) and (2) are shown in the partial formulas 33a and 34a. It can be seen from these changes that the differences between the spectra of the epimers amounts mainly to differences in the CSs of the geminal methyl group.

Great attention has been devoted in the literature to the study of the $^{13}C$ NMR spectra of glycyrrhetic acid and related compounds (45-60) [20, 21]. As can be seen from the spectra given, a change in the C-20 configuration, as in the cases (33, 34), causes appreciable changes only in the screening of the carbon atoms of ring E [20]. The C-29 resonances at 28.1 and 28.3 ppm in the spectra of compounds (45) and (47) are replaced by signals at 19.3 and 19.4 ppm in the spectra of (46) and (48). NMR spectroscopy has also proved useful for determining the 18α- and 18β- isomers of these acids [21]. Even in the case of a variation of the substituents at C-3, C-11, and C-20 the diagnostically valuable differences in the C-12, C-13, C-16, C-18, C-19, C-22, C-27, C-28, C-29, and C-30 resonances in the spectra of the 18α- and 18β-series remain unchanged. The most appreciable differences are shown by

TABLE 3. $^{13}$C NMR Spectra of Compounds (17)-(24)

| C | 17$^{C}$ | 18$^{C}$ | 19$^{C}$ | 20$^{C}$ | 21$^{C}$ | 22$^{C}$ | 23$^{C}$ | 24$^{C}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 46.4 | 41,7 | 38.0 | 38,8 | 39,1 | 39,7 | 38.8 | 39,2$^{a}$ |
| 2 | 68,8 | 66.5 | 26.0 | 23,5 | 27,3 | 34,1 | 23.6 | 27,3 |
| 3 | 83,8 | 78,9 | 71,8 | 80,6 | 78,6 | 216,8 | 80,6 | 78,7 |
| 4 | 39,1 | 38,5$^{a}$ | 55,2 | 38.0 | 39,1 | 47,6 | 38,1 | 39.2$^{a}$ |
| 5 | 55,3 | 48,1 | 48,0 | 55.1 | 55,0 | 55,3 | 55,2 | 55.1 |
| 6 | 18,3 | 18,1 | 20,7 | 17,3 | 17,4 | 18,7 | 17,5 | 17,6 |
| 7 | 32,6 | 32,5 | 32,3 | 32,9 | 32,9 | 32,2 | 33,9$^{a}$ | 34,0$^{b}$ |
| 8 | 39,1 | 39.7$^{a}$ | 39,6 | 43.5 | 43,5 | 43,6 | 43,7 | 43.7 |
| 9 | 47.5 | 47,4 | 47,5 | 61,7 | 61,8 | 61,0 | 60,7 | 60.8 |
| 10 | 38.3 | 38,3$^{a}$ | 36,0 | 37,2 | 37,3 | 36,8 | 36,9 | 37.1 |
| 11 | 23.1 | 23.4 | 23,0 | 199,9 | 200,2 | 199 3 | 199,5 | 199.8 |
| 12 | 122.0 | 122,1 | 121.9 | 127,9 | 127,9 | 127,7 | 123,2 | 123.2 |
| 13 | 143,6 | 143,8 | 143,6 | 168,5 | 168,5 | 169,0 | 165.7 | 165.7 |
| 14 | 41,7 | 41,9 | 41,7 | 45,0 | 45.0 | 44,8 | 44,9 | 44.9 |
| 15 | 27,6 | 27,7 | 27,6 | 27,8$^{a}$ | 27,7$^{a}$ | 27.8 | 28,1$^{b}$ | 27,7$^{c}$ |
| 16 | 23.5 | 23,2 | 23,3 | 23,0 | 23,0 | 22,9 | 34,0$^{a}$ | 34.0$^{b}$ |
| 17 | 46,6 | 46,8 | 46,6 | 46.2 | 46,2 | 46,1 | 50,0 | 50.0 |
| 18 | 41,3 | 41.3 | 41.3 | 41,6 | 41,6 | 41,6 | 33,3 | 33.3 |
| 19 | 45,8 | 46 0 | 45,8 | 44,3 | 44,3 | 44,3 | 38,8 | 39.1$^{a}$ |
| 20 | 30,7 | 30.7 | 30,7 | 30,7 | 30,7 | 30,6 | 30.8 | 30.8 |
| 21 | 33,8 | 34,0 | 33,8 | 33.7 | 33,7 | 33,6 | 34,0$^{a}$ | 34,1$^{b}$ |
| 22 | 32,3 | 32.5 | 32,1 | 31,6 | 31,6 | 31,5 | 35,8 | 35.7 |
| 23 | 28,6 | 28.5 | 207,0 | 28,1$^{a}$ | 28,1$^{a}$ | 26,5 | 27,7$^{b}$ | 28.1$^{c}$ |
| 24 | 16,8 | 21,9 | 8,9 | 16,7 | 15,6 | 21,3 | 16,7$^{c}$ | 15,7 |
| 25 | 16.8 | 16,4 | 15.5 | 16,2 | 16,2 | 15,5 | 16,6$^{c}$ | 16.5 |
| 26 | 16,8 | 17,0 | 16,8 | 19,0 | 19.0 | 18,7 | 18,4 | 18,4 |
| 27 | 26,0 | 26.2 | 26.0 | 23,0 | 23,6$^{b}$ | 23,4 | 21,0 | 21.0 |
| 28 | 178.0 | 178,1 | 177,9 | 177,3 | 177.4 | 177.3 | 174,9 | 175.1 |
| 29 | 33.1 | 33,2 | 33,1 | 32.9 | 32,9 | 32,8 | 25,1 | 25.1 |
| 30 | 23 5 | 23.6 | 23,6 | 23,5 | 23,4$^{b}$ | 23,4 | 40,0 | 40.0 |
| OMe | 51.5 | 51,5 | 51,5 | 51,8 | 51.8 | 51,8 | 51,2 | 51 .3 |
| OAc |  |  |  | 170,7<br>21,2 |  |  | 170,8<br>21,2 |  |

the signals of the olefinic carbon atoms in the two series of diastereomeric compounds. In the 18α-series, the C-12 signal is shifted upfield by 4.5-5 ppm, and the C-13 signal upfield by 2-4 ppm. The CSs of both olefinic atoms in both series are independent of the nature of the substitution at C-3 and C-20. The CSs of the C-18 signal are sensitive to a change in the configuration of the carbon atom. Regardless of the nature of the substituents at C-3, C-11, and C-20, the C-18 CS is 7-8 ppm lower in the 18α-series than in the 18β-series. In addition to this, the C-28 signal in the case of the 18β-compound is present in a weaker field and (as compared with the 18α-series) by approximately 12 ppm.

$^{13}$C NMR spectra have been used in the determination of the C-20 stereochemistry in the structures of imberbic acid (72) [24] and also those of the products of the oxidation of 3β-acetoxyolean-12-en-30-oic acid (68 and 69) [23].

Two new triterpenoids, called manevalic acid (79) and azizic acid (80) have been isolated from the plant Cornulaca monocantha [26]. Another series of compounds of oleanane nature with a carboxy group at C-14 has been isolated from Cordia alliogora (81), (85), (88), (90), (92) [27]. $^{13}$C NMR spectroscopy was widely used in the determination of their structures. According to Chen et al. [27], the changes in the CSs of the carbon atoms on the replacement of the methyl group at C-14 by a carboxy group showed the partial structure 87a. As can be seen from the tables, these results differ from those of Damidar et al. [26]. Since the structure of compound (91) was established by x-ray structural analysis, the results given in [27] apparently deserve greater confidence.

The effects of the substitution of oleanane derivatives at C-16 in compounds (95-97) and (99) were discussed in detail by Wehrli and Nishida [1]. The effects of the replacement of the C-30 methyl group by an aldehyde group in cyclamiretin D (104) [31] are shown in partial formula 104a.

Since ring E in oleanolic acid is present in the chair form [60] the directions of the changes in the CSs of the carbon atoms on the introduction of single hydroxy substituents into the C-19, C-21, and C-22 positions should be predictable on the basis of the laws given by Beirbeck et al. [5]. Partial formulas 105a, 116a, 112a, 114a, and 129a show the effects of the substitution of ring E by a hydroxy group according to the literature [1, 36, 14, 34,

TABLE 4. $^{13}$C NMR Spectra of Compounds (25)-(32)

| C | $25^{C}$ | $26^{C}$ | $27^{C}$ | $28^{P}$ | $29^{C}$ | $30^{C}$ | $31^{C}$ | $32^{C}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 39,7 | 38,7 | 38,3 | 37,6 | 38,5 | 38,7 | 39,4 | 38,5 |
| 2 | 34,1$^{a}$ | 23,4 | 26,0 | 26.2 | 27,2 | 27,0 | 34,6 | 23,7 |
| 3 | 216,9 | 80,5 | 75,7 | 74,0 | 79,1 | 78,9 | 217,7 | 81,1 |
| 4 | 47.6 | 38,0 | 41.7 | 53,0 | 38.8 | 38,7 | 47,5 | 37,9 |
| 5 | 55,3 | 54,9 | 49,3 | 50,5 | 55,3 | 55.3 | 55,4 | 55,5 |
| 6 | 18,8 | 18,4 | 18,3 | 20,2 | 18,4 | 18,5 | 19,6 | 18,4 |
| 7 | 33,2 | 32,6 | 32,3 | 31,5 | 32,7 | 32,8 | 32,1 | 32.4 |
| 8 | 43,5 | 43,3 | 39,7 | 38,6 | 39,3 | 39,3 | 39,9 | 40,0 |
| 9 | 60,0 | 61,5 | 47,4 | 46,9 | 47,7 | 47,7 | 46.8 | 47,7 |
| 10 | 36,6 | 36,9 | 36,8 | 35,3 | 37,1 | 37.2 | 36,7 | 37,0 |
| 11 | 198,9 | 201,4 | 23,6 | 22.3 | 23,1 | 23,4 | 23,8 | 23.7 |
| 12 | 123,0 | 127,9 | 122,1 | 122,4 | 122,8 | 122,8 | 123,3 | 123,6 |
| 13 | 166,1 | 170.2 | 144.2 | 143,3 | 143,2 | 143,2 | 143,2 | 143,1 |
| 14 | 44,9 | 45.3 | 41,7 | 40,7 | 41,6 | 41,7 | 41,8 | 41,8 |
| 15 | 27,7 | 26.4 | 25,6 | 26,8 | 27,7 | 27,7 | 25,5 | 25,7 |
| 16 | 33,9$^{a}$ | 26,4 | 21,9 | 22,2 | 23,5 | 23,4 | 22,4 | 22,9 |
| 17 | 50,0 | 32,3 | 36.8 | 45,1 | 47,0 | 46.8 | 38,1 | 35,9 |
| 18 | 33,2 | 47,5 | 42,5 | 40,5 | 40,5 | 40,3 | 41,6 | 42,0 |
| 19 | 39,7 | 45.0 | 46,6 | 45.0 | 40,1 | 40,3 | 40,6 | 41,8 |
| 20 | 30,7 | 31,0 | 30,9 | 29,5 | 35,8 | 35,2 | 34,2 | 34,2 |
| 21 | 34,1$^{a}$ | 34,4 | 34,2 | 32.7 | 31,6 | 32,8$^{a}$ | 28,7 | 29,6 |
| 22 | 35,7 | 36,4 | 30,9 | 31,5 | 32,7 | 32,1$^{a}$ | 30,3 | 30,9 |
| 23 | 26,5 | 28 0 | 70,3 | 179,2 | 28,1 | 28,1 | 26,5 | 28,0 |
| 24 | 21,3$^{b}$ | 16.6 | 11,6 | 10,7 | 15,6 | 15,7 | 21,6 | 16,9 |
| 25 | 15,8 | 15,7 | 15.9 | 14,5 | 15,3 | 15,4 | 15,3 | 15,7 |
| 26 | 18,2 | 17,3 | 16,7 | 15,9 | 16,9 | 16,9 | 16,7 | 16.9 |
| 27 | 21.0$^{b}$ | 23,5 | 26,0 | 24,7 | 25,9 | 26,0 | 25,9 | 26,1 |
| 28 | 174,8 | 28,7 | 69,1 | 178,7 | 178,1 | 178,5 | 70.4 | 70,3 |
| 29 | 25,1 | 33,0 | 33,2 | 31,8 | 74,4 | 28,9 | 74,9 | 28,2 |
| 30 | 40,1 | 23,5 | 23,6 | 22,3 | 19,0 | 65,8 | 19,2 | 67,9 |
| OMe | 51,3 |  |  |  | 51,6 | 50,6 |  |  |
| OAc |  | 170,6<br>21,2 |  |  |  |  |  |  |

40]. It can be seen from these figures that the influence of hydroxy substituents on the CSs does not extend further than ring E itself and one or two carbon atoms of ring D. These characteristics were widely used in [36] for determining the structures of kudzusapongenol C (118), kudzusapogenol A (121), and the methyl ether of kudzusapogenol B (122).

Two cytotoxic sapogenols, (125) and (126), have been isolated from an acid hydrolysate of a crude mixture of saponins from *Aesculus hippocastanum* [39]. The position of the ester group in compound (126) was determined from the acylation shifts in its $^{13}$C NMR spectrum as compared with the spectrum of the product of its alkaline hydrolysis (128), which amounted to +3.4 ppm for C-21 and −3.9 ppm for C-22.

Homoannular dienes of the oleanane series (149 and 150) have been isolated by Diaz et al. [47]. $^{13}$C NMR spectroscopy was used to establish the position of the hydroxy substituent in (150) from the β-effects in the spectrum of its keto derivative (151), which were assumed to be similar to the β-effects of the analogous substituent in 6-oxosteroids [48].

The structure of moronic acid (153) was established by a comparison of it with the known morolic acid (154) [49]. In the hypothetical migration of the double bond from the C-12—C-13 position into the C-18—C-19 position the C-27 and C-29 signals undergo an upfield shift, while the C-16 and C-30 signals undergo a downfield shift. Subsequently, another two papers with information on the spectra of olean-18-ene derivatives [50, 51] were published.

The γ-lactone (172) was isolated from *Pieris japonica* D. Don [52]. The assignment of the signals in the spectra of compounds (172-174) was made on the basis of experiments with incomplete and selective decoupling from protons and by comparison with the spectra of similar compounds.

On the acid hydrolysis of the glycosidic fraction from the epigeal part of *Androsace saxifragifolia*, androsacenol (177) was detected [31], and the configuration of the C-16 group in it was established by comparing its $^{13}$C NMR spectra with those of analogously substituted saikogenins.

TABLE 5. $^{13}C$ NMR Spectra of Compounds (33)-(40)

| C | 33-D | 34-C | 35-D | 36-D | 37C | 38-C | 39-C | 40C |
|---|---|---|---|---|---|---|---|---|
| 1 | 33,2 | 38,5 | 43,3 | 37,8 | 43,8 | 41,6 | 41,9 | 41,9 |
| 2 | 25,3 | 27 2 | 70,9 | 70,4 | 71,2 | 69,6 | 69,6 | 69,7 |
| 3 | 70,6 | 79 0 | 79,1 | 77,0 | 72,7 | 72,0 | 78,0 | 72,1 |
| 4 | 42,7 | 38,7 | 42,2 | 36,5 | 41,7 | 40,1 | 37,3 | 40,2 |
| 5 | 49,6 | 55,2 | 47,7 | 54,9 | 48,4 | 48,2 | 55,3 | 48.3 |
| 6 | 18,7 | 18,3 | 17,6 | 17,8 | 18,1 | 17,7 | 18,0 | 17,7 |
| 7 | 33,0 | 32,7 | 32,2 | 29,8 | 32,5 | 32,3 | 32,5 | 32,7 |
| 8 | 40,0 | 39,3 | 40,7 | 41,4 | 39,5 | 39,4 | 39,1 | 39,4 |
| 9 | 47,1 | 47,6 | 47,4 | 47,5 | 48,4 | 47,8 | 48,1 | 47,8 |
| 10 | 36,9 | 37,0 | 36,4 | 32,5 | 36,7 | 36,7 | 36,8 | 36,8 |
| 11 | 23,7 | 23,2 | 22,8 | 22,8 | 23,4 | 23,0 | 23,0 | 23,0 |
| 12 | 122,4 | 123,4 | 122,1 | 122,1 | 123,2 | 123,1 | 123,2 | 123,1 |
| 13 | 143,8 | 142,8 | 143,7 | 143,6 | 143,3 | 143,1 | 143,1 | 143,6 |
| 14 | 41,2 | 41,6 | 40,7 | 41,6 | 41,2 | 41,6 | 41,8 | 41,6 |
| 15 | 27,8 | 28,3 | 27,2 | 23,0 | 27,7 | 27,5 | 27,6 | 27,6 |
| 16 | 23,2 | 23,4 | 23,1 | 22,8 | 23,5 | 23,4 | 23,4 | 23,4 |
| 17 | 45,9 | 46,4 | 45,1 | 45,0 | 46,2 | 45,9 | 45,9 | 45,9 |
| 18 | 42,7 | 40,2 | 41,7 | 43,3 | 42,7 | 42,3 | 42,3 | 42,3 |
| 19 | 41,3 | 39,7[a] | 41,3 | 42,2 | 42,2 | 42,0 | 42,0 | 42,0 |
| 20 | 44,0 | 42,2[a] | 43,8 | 43,9 | 43,9 | 43,7 | 43,7 | 43,7 |
| 21 | 30,6 | 27,[illegible][a] | 29,8 | 29,6 | 30,5 | 30,3 | 30,3 | 30,5 |
| 22 | 33,6 | 31,2 | 33,3 | 33,3 | 33,5 | 33,5 | 33,6 | 33,7 |
| 23 | 21,7 | 28,1 | 66,3 | 27,1 | 68,5 | 65,6 | 28,3 | 65,7 |
| 24 | 66,5 | 15,6[b] | 13,5 | 16,9 | 13,4 | 13,7 | 16,0 | 13,8 |
| 25 | 15,6 | 15,3[b] | 16,5 | 16,0 | 16,8 | 16,5 | 17,3 | 16,6 |
| 26 | 16,7 | 16,8 | 16,7 | 17,5 | 16,8 | 17,2 | 17,6 | 17,2 |
| 27 | 25,4 | 26,0 | 25,4 | 25,6 | 25,9 | 25,8 | 26,0 | 25,9 |
| 28 | 178,9 | 177,9 | 178,8 | 176,5 | 177,6 | 182,8 | 176,9 | 176,9 |
| 29 | 27,9 | 177,2 | 27,9 | 27,9 | 28,4 | 28,3 | 29,1 | 28,3 |
| 30 | 176,5 | 19,3 | 176,5 | 178,3 | 177,0 | 176,9 | 183,2 | 182,7 |
| OMe | 51,5 | 51,7 | 51,7 | 51,6 | 51,6 | 51,7 | 51,7 | 51,7 |
| OAc | | | 170,4<br>20,7 | | 171,0<br>20,9 | 170,0<br>170,3<br>170,7<br>20,7<br>20,8<br>21,2 | 170,6<br>170,1<br>20,8<br>21,2 | 170,7<br>170,0<br>170,2<br>20,7<br>21,7<br>20,8 |

TABLE 6. $^{13}C$ NMR Spectra of Compounds (41)-(48)

| C | 41-C | 42-C | 43C | 44 | 45C | 46C | 47C | 48-C |
|---|---|---|---|---|---|---|---|---|
| 1 | 37,8 | [illegible] | 38,2 | 44,8 | 38,9 | 39,0 | 38,5 | 38,4 |
| 2 | 23,1 | [illegible] | 23,6 | 71,5 | 23,7 | 23,6 | 23,6 | 23,6 |
| 3 | 74,7 | 79,1 | 81,0 | 73.0 | 80,7 | 80,8 | 81,1 | 81,1 |
| 4 | 40.7 | 38,8 | 37,8 | 42,4 | 37,9 | 38,1 | 37,8 | 37,8 |
| 5 | 48,1 | 55,4 | 55,5 | 48,1 | 55,2 | 55,1 | 55,5 | 55,4 |
| 6 | 18,0 | 18,3 | 18,3 | 18,2 | 17,5 | 17,5 | 18,4 | 18,3 |
| | 32,4 | 32,7 | 32-7 | 33,0 | 32,8 | 32,8 | 32,7 | 32,7 |
| | 39,4 | 39,4 | 39,4 | 39,8 | 43,3 | 43,5 | 39,9 | 39,9 |
| | 47,8 | 47,7 | 47,7 | 48,5 | 61,9 | 61.9 | 47,7 | 47,6 |
| | 36,9 | 37 2 | 37,1 | 37,2 | 37,1 | 37,1 | 37,0 | 37,0 |
| | 23,0 | 23,2 | 23,2 | 23,9 | 200,2 | 200,2 | 23,6 | 23,6 |
| | 123,3 | 123 4 | 123,4 | 123,3 | 128,9 | 128,9 | 122,8 | 123,0 |
| 13 | 143,1 | 143,0 | 143,0 | 144,4 | 169,3 | 169,3 | 144,7 | 144,4 |
| 14 | 41,5 | 41,5 | 41,6 | 42,2 | 45,5 | 45,5 | 41,7 | 41.7 |
| 15 | 27,7 | 27,8 | 27,8 | 28,4 | 26,6 | 26,4 | 26,3 | 26,6 |
| 16 | 23,4 | 23,4 | 23,4 | 23,9 | 26,6 | 26,4 | 27,1 | 27,0 |
| 17 | 46,0 | 46,0 | 46,0 | 46,1 | 31,9 | 32,4 | 32,1 | 32,5 |
| 18 | 42,4 | 42,3 | 42,4 | 43,3 | 48,5 | 46,4 | 48,4 | 46,1 |
| 19 | 42,1 | 42,1 | 42,2 | 42,7 | 41,3 | 39,0 | 43,0 | 40,6 |
| 20 | 43,8 | 43,7 | 43,8 | 44,1 | 44,1 | 42,5 | 44,4 | 42,8 |
| 21 | 30,4 | 30 4 | 30,5 | 30,8 | 31,2 | 29,0 | 31,4 | 29,1 |
| 22 | 33,6 | 33 6 | 33,6 | 34,5 | 38,2 | 35,4 | 38,6 | 36,0 |
| 23 | 65.6 | 28,1 | 28,1 | 67,7 | 28,3[a] | 28,1[a] | 28,3[a] | 28,3[a] |
| 24 | 13,0 | 15.4 | 16,7 | 14,5 | 16,7[b] | 16,7[b] | 16,8 | 16,8 |
| 25 | 15,8 | 15,5 | 15,5 | 17,4 | 16,4[b] | 16,4[b] | 15,6 | 15,6 |
| 26 | 17,1 | 17,2 | 17,2 | 17,2 | 18,8 | 18,8 | 16,8 | 16,8 |
| 27 | 25,8 | 25,9 | 29,9 | 26,2 | 23,4 | 23,4 | 26.0 | 26,0 |
| 28 | 176,9 | 183,1 | 183,1 | 179,7 | 28,6[a] | 28,6[a] | 28,6[a] | 28,2[a] |
| 29 | 28 4 | 28,4 | 28,4 | 28,4 | 28,1[a] | 178,9 | 28,3[a] | 179,6 |
| 30 | 183,0 | 176,9 | 170,0 | 177,1 | 177,8 | 19,3 | 177,9 | 19,4 |
| OMe | 51,7 | 51,8 | 51,8 | 51,6 | 51,7 | 52,7 | 51,6 | 51,8 |
| OAc | 170,7<br>170,9<br>21,1<br>20,8 | | 171,0<br>21,3 | | 171,1<br>21,2 | 171,2<br>21,3 | 171,1<br>21,3 | 171,2<br>21.3 |

TABLE 7. $^{13}C$ NMR Spectra of Compounds (49)-(56)

| C | 49[C] | 50[C] | 51[C] | 52[C] | 53[C] | 54[C] | 55[C] | 56[C] |
|---|---|---|---|---|---|---|---|---|
| 1 | 39,0 | 39,6 | 38.6 | 38,5 | 38,2 | 38,7 | 38,8 | 39,1 |
| 2 | 27,2 | 34,0 | 27,2 | 27,2[a] | 23,6 | 23,5 | 23.5 | 27,1 |
| 3 | 78.3 | 215,8 | 78,8 | 78,8 | 80,6 | 80,3 | 80,5 | 78,3 |
| 4 | 39,0 | 47,5 | 38.6 | 38,7 | 37,6 | 37.9 | 37,9 | 39,0 |
| 5 | 54,8 | 55,2 | 55.1 | 55,1 | 55,1 | 54,9 | 55,0 | 54.9 |
| 6 | 17,5 | 18,8 | 18,4 | 18,4 | 18,2 | 17,5 | 17,5 | 17,5 |
| 7 | 32,7 | 32,0 | 32,7 | 32,7 | 32,6 | 33,7 | 33,4 | 33,7 |
| 8 | 43,1 | 43,2 | 39,7 | 39,7 | 39,7 | 43,7 | 43,8 | 43.7 |
| 9 | 61,6 | 60,8 | 47,6 | 47,6 | 47,4 | 60,4 | 60,5 | 60.5 |
| 10 | 37.0 | 36.6 | 36,9 | 36,8 | 36.8 | 36.7 | 36,7 | 36,8 |
| 11 | 199,2 | 198,4 | 23,4 | 23,5 | 23,6 | 198,5 | 199,4 | 198,8 |
| 12 | 128.1 | 127,9 | 122,2 | 122,1 | 121,9 | 123,7 | 124,0 | 123,6 |
| 13 | 168,3 | 168,8 | 143,9 | 144,4 | 143,9 | 164,8 | 165.6 | 164,9 |
| 14 | 45,2 | 45,0 | 41,5 | 41,7 | 41 6 | 44,8 | 44,8 | 44,8 |
| 15 | 26,4 | 26,4 | 26,1 | 26,1 | 26,0 | 26,7 | 26,8 | 26,6 |
| 16 | 26,4 | 26.4 | 27,0 | 27,3[a] | 27,1 | 37,5 | 37,6 | 37.5 |
| 17 | 31,7 | 31,7 | 31,9 | 32,4 | 32,3 | 35,3 | 35,0 | 35,3 |
| 18 | 48.2 | 48,2 | 48,1 | 46.7 | 46,5 | 40,3 | 42,7 | 40,3 |
| 19 | 41,0 | 41,1 | 42,8 | 41,9 | 42,1 | 35,9 | 38,4 | 35,9 |
| 20 | 43,9 | 43,8 | 44,1 | 35,5 | 34,1 | 42 5 | 44,2 | 42.4 |
| 21 | 31,1 | 31,0 | 31,3 | 29,6 | 30 1 | 31,7 | 33,7 | 31,7 |
| 22 | 37,7 | 37,7 | 38,3 | 36,5 | 36.4 | 28,4 | 30,7 | 28.4 |
| 23 | 28,1 | 26,4 | 28,1 | 28,1 | 28,0 | 28,0 | 28,0[a] | 28,0 |
| 24 | 15,6 | 21,3 | 15,3[a] | 15,5 | 16,6[a] | 16,7[a] | 16,6[b] | 15,7 |
| 25 | 16,2 | 15,5 | 15,5[a] | 15.5 | 15.5 | 16,5[a] | 16,2 | 16,4 |
| 26 | 18,6 | 18,4 | 16,8 | 16,8 | 16,8[a] | 18,5 | 18,5 | 18,5 |
| 27 | 23,2 | 23.2 | 25 9 | 25,9 | 25,9 | 20,6 | 20,6 | 20,6[a] |
| 28 | 28,1 | 28,1 | 28,1 | 28.1 | 28,0 | 15,9 | 16,8[b] | 15,9 |
| 29 | 28,4 | 28,4 | 28,4 | 29,6 | 28,0 | 20.6 | 177,2 | 20.7[a] |
| 30 | 176,1 | 176,0 | 176.9 | 66,6 | 67,8 | 177,9 | 28,6[a] | 178,0 |
| OMe | 51.4 | 51.4 | 51.3 |  |  | 51,6 | 51,7 | 51,6 |
| OAc |  |  |  |  |  | 170,1<br>21,2 | 170,7<br>21,2 |  |

TABLE 8. $^{13}C$ NMR Spectra of Compounds (57)-(64)

| C | 57[C] | 58[C] | 59[C] | 60[C] | 61[C] | 62[C] | 63[C] | 64[C] |
|---|---|---|---|---|---|---|---|---|
| 1 | 39.6 | 38,8 | 38,2 | 38,5 | 38,8 | 38,8 | 38,8 | 38.8 |
| 2 | 34,0 | 27,2 | 27,2 | 23,6 | 23,6 | 23,5 | 23.5 | 23,5 |
| 3 | 215,9 | 78,6 | 78.8 | 80,6 | 80,5 | 80,5 | 80,6 | 80.6 |
| 4 | 47,5 | 38,7 | 38,7 | 37,7 | 38,0 | 38 0 | 38.0 | 38,0 |
| 5 | 55,3 | 55,2 | 55,2 | 55,3 | 55.0 | 55,0 | 55,0 | 55,0 |
| 6 | 18,9 | 18,3 | 18,3 | 18,2 | 17,4 | 17,4 | 17.4 | 17,4 |
| 7 | 33,1 | 33,1 | 34,1 | 34.0 | 32,7 | 32,7 | 32.7 | 32,7 |
| 8 | 43,6 | 39,5 | 39,5 | 39,5 | 43,1 | 43.2 | 43.3 | 43,4 |
| 9 | 59,8 | 47,2 | 47,2 | 47,1 | 61,7 | 61,3 | 61,7 | 61,7 |
| 10 | 36,4 | 36.8 | 36,8 | 36,7 | 36,9 | 36,9 | 36,9 | 36,9 |
| 11 | 198,1 | 23.2 | 23,1 | 23,1 | 199,7 | 199,6 | 199,7 | 200,4 |
| 12 | 123,7 | 117,2 | 116,9 | 116,9 | 128,8 | 128,6 | 128,4 | 128,0 |
| 13 | 165,3 | 141,5 | 141,9 | 142,0 | 167,7 | 168,1 | 168.6 | 170.1 |
| 14 | 44,9 | 43,6 | 43,6 | 43,6 | 45,4 | 45,4 | 45,4 | 45,5 |
| 15 | 26,7 | 26,3 | 26,3 | 26,3 | 26,4 | 26.3 | 26,4 | 26,2 |
| 16 | 37,5 | 38,1 | 38,8 | 38,1 | 26,3 | 26,2 | 26,3 | 26,2 |
| 17 | 35,4 | 34,9 | 35,3 | 35,1 | 31.9 | 31,9 | 31,9 | 31,8 |
| 18 | 40,3 | 39,3 | 39,6 | 39,5 | 47,7 | 47,2 | 46,7 | 46,6 |
| 19 | 35,9 | 36,0 | 36,3 | 36.1 | 41,5 | 44,5 | 41,9 | 43,2 |
| 20 | 42,5 | 42,8 | 36,2 | 34,8 | 54,4 | 58.6 | 52.4 | 52,6 |
| 21 | 31,7 | 32,4 | 32,3 | 32.6 | 31,6 | 34,8 | 31,9 | 30,5 |
| 22 | 28,4 | 28,7 | 28,5 | 28,8 | 37,1 | 36,2 | 35.6 | 35,9 |
| 23 | 26,4 | 28,1 | 28,1 | 28,0 | 28.0 | 28.0 | 28,1 | 28,1 |
| 24 | 21,4 | 15,2 | 15,2 | 16,8 | 16,7 | 16,7 | 16.7 | 16,7 |
| 25 | 15,7[a] | 15,7 | 15,7 | 15,2 | 16,4 | 16,4 | 16.4 | 16,4 |
| 26 | 18,4 | 15,8 | 15,8 | 15,9 | 18,7 | 18,7 | 18.7 | 18.6 |
| 27 | 20,7 | 23,2 | 23,1 | 23.1 | 23,4 | 23,3 | 23,3 | 23,2 |
| 28 | 16,0[a] | 17,4 | 17,4 | 17,4 | 28.3 | 28.2 | 28,2 | 28,1 |
| 29 | 20,7 | 20,9 | 20,6 | 20,8 | 27,4 | 31,7 | 28,3 | 28,5 |
| 30 | 177,9 | 178,7 | 74,9 | 75,0 | 179,0 | 122,2 | 155,3 | 155,7 |
| OMe | 51,6 | 51,5 |  |  |  |  | 51,6 |  |
| OAc |  |  |  |  | 170.9<br>21.3 | 170,8<br>21.2 | 170,9<br>21,3 |  |

TABLE 9. $^{13}C$ NMR Spectra of Compounds (65)-(72)

| C | $65^{C}$ | $66^{C}$ | $67^{C}$ | $68^{C}$ | $69^{C}$ | $70^{C}$ | $71^{C}$ | $72^{P}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 1 | 38,5 | 40,9 | 37,8 | 35,9 | 35,9 | 37,1 | 35.8 | 72,8 |
| 2 | 23,5 | 18,4 | 23,4 | 23,5 | 23,5 | 24,0 | 23,6 | 35,9 |
| 3 | 80,4 | 42.0 | 80,5 | 79,2 | 79,2 | 80 3 | 79,3 | 71,9 |
| 4 | 37,8 | 33,4 | 38,1 | 37 8 | 37,8 | 37,7 | 37.8 | 40,1 |
| 5 | 54,9 | 55,7 | 54.7 | 50,5 | 50.5 | 51,7 | 50 0 | 48,6 |
| 6 | 18,2 | 17,7 | 17,8 | 17,4 | 17,4 | 17,9 | 17.6 | 17,4 |
| 7 | 32,7 | 32,8 | 33,2 | 33.8 | 33,7 | 32.0 | 33 6 | 33,0 |
| 8 | 43,4 | 43.2 | 42,7 | 45,0 | 44.9 | 44.0 | 45,2 | 39,8 |
| 9 | 45,7 | 61,9 | 63,3 | 179,5 | 179.0 | 153,2 | 176,8 | 38,4 |
| 10 | 34,2 | 37,3 | 36,7 | 40,0 | 40,0 | 38,6 | 39,4 | 42,7 |
| 11 | 70,4 | 200,4 | 208,8 | 121,9 | 121,9 | 117,1 | 122,8 | 23.8 |
| 12 | 121 2 | 128,6 | 44,6 | 187.7 | 187,7 | 26,5 | 200.6 | 123.7 |
| 13 | 150,5 | 168,7 | 132,7 | 139,6[a] | 138,2[a] | 30,6 | 47,6 | 144,7 |
| 14 | 41,5 | 42,6 | 37,8 | 44,9 | 44,8 | 38,3 | 41.5 | 41,7 |
| 15 | 26,8 | 26,4 | 25,7 | 25,0 | 25,1 | 27,0 | 26,0 | 26,7 |
| 16 | 26,2 | 26,4 | 25,7 | 33.1 | 33,1 | 27.0 | 26,0 | 27,5 |
| 17 | 32,0 | 31,8 | 34,6 | 41.6 | 41,0 | 32,3 | 31,7 | 33,0 |
| 18 | 52,1 | 48 4 | 132,3 | 150,7[a] | 151,7[a] | 41.7 | 37.7 | 46,8 |
| 19 | 42,1 | 41,1 | 36,1 | 206,2 | 203 9 | 33,4 | 32,6 | 41,8 |
| 20 | 37,9 | 44,0 | 44,2 | 59,2 | 58,4 | 43,7 | 43,7 | 43,0 |
| 21 | 29,7 | 31,1 | 32,8 | 31 9 | 34,6 | 30,9 | 31,0 | 30,0 |
| 22 | 36.3 | 37,8 | 36,1 | 36,1 | 37,3 | 38,9 | 38,0 | 36,7 |
| 23 | 28,0 | 33,6 | 28,0 | 27,6 | 27,7 | 27,4 | 27,7 | 28,6 |
| 24 | 16,4 | 21,8 | 16,7 | 16,4 | 16.5 | 16,3 | 16,4 | 16 8 |
| 25 | 17,2 | 16,3 | 16,3 | 24,4 | 24,4 | 24.8 | 23,7 | 16,6 |
| 26 | 18,2 | 18,8 | 18,8 | 22 1 | 22 0 | 18,4 | 41,7 | 16,6 |
| 27 | 25,5 | 23,4 | 23,9 | 26,2 | 26,1 | 25,2 | 23,7 | 26.3 |
| 28 | 28,0 | 28,3 | 19,7 | 22,2 | 22,8 | 27,8 | 26,8 | 29,0 |
| 29 | 28,2 | 28,5 | 28,0 | 172,9 | 20,0 | 28,7 | 28,3 | 181,4 |
| 30 | 67,7 | 176,8 | 178,6 | 18,5 | 171,4 | 177,3 | 177,2 | 18,9 |
| OMe |  | 51,7 | 51,8 | 51,8 | 52,0 | 51.2 | 51,1 |  |
| OAc | 170,9 |  | 170,9 | 170,4 | 170.3 | 170,5 | 170,1 |  |
|  | 171,2 |  | 21,3 | 20,9 | 20.9 | 21.0 | 20,8 |  |
|  | 21.3 |  |  |  |  |  |  |  |
|  | 20,9 |  |  |  |  |  |  |  |

TABLE 10. $^{13}C$ NMR Spectra of Compounds (73)-(80)

| C | $73^{C}$ | $74^{C}$ | $75^{C}$ | $76^{C}$ | $77^{C}$ | $78^{C}$ | $79^{C}$ | $80^{C}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 75.9 | 75 8 | 210,9[a] | 45,3 | 45,5 | 44,2[a] | 38,2 | 33,1 |
| 2 | 27,6 | 27.6 | 51,2 | 35,3 | 32.1 | 42,6 | 26,7 | 26,7 |
| 3 | 74,1 | 74.1 | 208,3[a] | 79,8 | 80,4 | 221,3 | 76 8 | 76,6 |
| 4 | 37,6 | 37,6 | 47.1 | 44,1 | 43,7[a] | 49,8 | 41,8 | 43,7 |
| 5 | 49,0 | 49,1 | 49,2 | 51,7 | 51,6 | 52,0 | 49,8 | 49,7 |
| 6 | 17,9 | 18,0 | 19,1 | 21.1 | 20,9 | 21 1 | 71,9 | 71,8 |
| 7 | 31,8 | 31,8 | 31,5 | 34,8 | 34.7 | 35.3 | 32.5 | 32,5 |
| 8 | 39,5 | 39,5 | 39,8 | 44,0 | 44,0 | 44,2[a] | 39,4 | 39,3 |
| 9 | 38,0 | 38.0 | 37,6 | 62,1 | 61,8 | 58.5 | 47,6 | 47,6 |
| 10 | 39,8 | 39.9 | 51,0 | 143,8 | 143,5 | 146 2 | 36,9 | 36,9 |
| 11 | 22,9 | 22.9 | 25,8 | 198,3 | 198,0 | 198,9 | 25,9 | 25,9 |
| 12 | 122,2 | 122.1 | 123.4 | 128,3 | 128,3 | 128,4 | 122,3 | 123,0 |
| 13 | 143,8 | 143,9 | 142,6 | 171,0 | 171,6 | 172,4 | 143,8 | 143,1 |
| 14 | 41,7 | 41,8 | 42.0 | 44,1 | 44,0 | 44,3[a] | 51.4 | 51,7 |
| 15 | 25,8 | 25,8 | 26,6 | 26,6[a] | 26,6[b] | 26,5[b] | 29,6 | 29,6 |
| 16 | 26,6 | 26,7 | 26,9 | 28,2[a] | 28,2[b] | 28,2[b] | 23,4 | 28,3 |
| 17 | 32,1 | 32,2 | 32,4 | 31,7 | 31,6 | 31,6 | 26,7 | 51,4 |
| 18 | 45,6 | 45,6 | 46,2 | 48,7 | 48,7 | 48,5 | 41.7 | 42,5 |
| 19 | 40,1 | 40,2 | 39,8 | 41,8 | 41,8 | 42,2 | 45,9 | 46,1 |
| 20 | 42.4 | 42,6 | 42,4 | 47,6 | 42,6[a] | 43,6 | 30,6 | 30,4 |
| 21 | 28 7 | 29,0 | 28,8 | 31,1 | 31,1 | 31,2 | 33,9 | 42,1 |
| 22 | 35,6 | 35,7 | 35,6 | 37,7 | 37,7 | 37,8 | 32,4 | 41,5 |
| 23 | 27,7[a] | 27,8[a] | 28,8 | 27,1 | 27,2 | 26,9 | 27,7 | 27,7 |
| 24 | 16 4 | 16,4 | 20.3 | 16.8 | 16,8 | 20,5 | 16,9 | 16,8 |
| 25 | 15,6 | 15,6 | 13,0 | 115,7 | 115,8 | 117,5 | 15,6 | 15,6 |
| 26 | 16,6 | 16,7 | 17,4 | 16.8 | 17,1 | 17,9 | 18 5 | 18.4 |
| 27 | 25,8 | 25,8 | 25,3 | 23,8 | 23.8 | 24,7 | 178,3 | 177,1 |
| 28 | 27,9[a] | 27,9[a] | 28,0 | 28,2[a] | 28,2[b] | 28,3[b] | 15,6 | 177,6 |
| 29 | 184,8 | 179,2 | 184,7 | 28,6 | 28,6 | 28,7 | 33,0 | 33,5 |
| 30 | 18.9 | 19,1 | 19,0 | 176,8 | 176.7 | 176,8 | 23,6 | 23,3 |

TABLE 11. $^{13}C$ NMR Spectra of Compounds (81)-(88)

| C | 81[C] | 82[C] | 83[C] | 84[C] | 85[C] | 86[C] | 87[C] | 88[C] |
|---|---|---|---|---|---|---|---|---|
| 1 | 36,7[a] | 36,7[a] | 36,9[a] | 36,7[a] | 39,0 | 39,4 | 36,9 | 38,8 |
| 2 | 27,6 | 27,6 | 27.5 | 27,6 | 34,3 | 34,2 | 27,8 | 35,6 |
| 3 | 76,4 | 75.8 | 78,1 | 78,1 | 217,8 | 217,8 | 78.8 | 217,9 |
| 4 | 39,9 | 40,0 | 40,3 | 39,7 | 47,1 | 47,0 | 40,2 | 47,2 |
| 5 | 48,8 | 49.0 | 49,9 | 50,0 | 54,5 | 54,8 | 55,5 | 54,2 |
| 6 | 18,0 | 18,1 | 18,2 | 18,0 | 19,5 | 19,4 | 18,3 | 19,3 |
| 7 | 32,9 | 33,2 | 33,3 | 33,0 | 34,0 | 33,8 | 33,5 | 33.8 |
| 8 | 36,7 | 37,2 | 36,5 | 36,4 | 39.8 | 39,4 | 37,3 | 39,5 |
| 9 | 48,8 | 49,0 | 49,3 | 48,9 | 49,2 | 48,9 | 49,2 | 46,9 |
| 10 | 36,7[b] | 37,1 | 36,4[b] | 36.4 | 36,1[a] | 36,3 | 38,8 | 36.5 |
| 11 | 23,6[b] | 22,7[b] | 23,6[b] | 22,5 | 22,9[a] | 22,8[a] | 23,0[a] | 21,9[a] |
| 12 | 126,0 | 125,5 | 126.4 | 125 3 | 125,8 | 125.0 | 125,5 | 125,8 |
| 13 | 137,6 | 137,5 | 137.6 | 137,4 | 137,6 | 137,4 | 137,5 | 137,6 |
| 14 | 56,0[b] | 56,1[b] | 55.9[b] | 56,1 | 55,7 | 55,8 | 56.1 | 55,5 |
| 15 | 22,7[b] | 22.3[b] | 22,5[b] | 22.5 | 22,2[a] | 22,2[a] | 22,3[a] | 22,8[a] |
| 16 | 26,2 | 25,3 | 23,6 | 23,6 | 29.7 | 28.0 | 27,3 | 27,3 |
| 17 | 32,9 | 32,9 | 32,9 | 32,8 | 32,9 | 32,7 | 32.9 | 32,8 |
| 18 | 47,0 | 47,4 | 47,0 | 47,4 | 46,2 | 46,3 | 47,5 | 46,4 |
| 19 | 44,2 | 44,0 | 44,2 | 43,8 | 44,0 | 43,7 | 44,0 | 34,4 |
| 20 | 31,0 | 30,9 | 31,0 | 30,7 | 31,0 | 31,3 | 30,9 | 46,0 |
| 21 | 34,2[a] | 34,3[a] | 34,3[a] | 34,2 | 35.8 | 35,8 | 34,3 | 25,6 |
| 22 | 36,2[a] | 36,5[a] | 36,5 | 36,4 | 36,5 | 36,3 | 36,8 | 36,5 |
| 23 | 28,2 | 28,2 | 27,8 | 27,6 | 26,9 | 26,9 | 28,3 | 26,2 |
| 24 | 22,1 | 22,8 | 22,6 | 22,5 | 21,4 | 21.1 | 15.7 | 21,1 |
| 25 | 15,8 | 16,3 | 16,2 | 16,0 | 16.2 | 16.0 | 16,4 | 15,9 |
| 26 | 18.0 | 18,1 | 18,2 | 18,0 | 17,9 | 18,0 | 18,1 | 17,8 |
| 27 | 179,0 | 176.0 | 181,7 | 176,0 | 181,4 | 175,9 | 176,1 | 180.4 |
| 28 | 28,2 | 28.2 | 28,2 | 28,1 | 28,2 | 27,4 | 28,2 | 27,9 |
| 29 | 32,9 | 33,2 | 33,8 | 34,0 | 33,5 | 33,4 | 33,2 | 205,8 |
| 30 | 23,6 | 23,5 | 23,6 | 23,6 | 23,5 | 23,6 | 23,5 | 15,9 |
| OMe |  | 51,3 |  | 51.3 |  |  |  |  |
| OAc |  |  | 170,6<br>21,7 | 170,3<br>21,7 |  |  |  |  |

TABLE 12. $^{13}C$ NMR Spectra of Compounds (86)-(96)

| C | 89[C] | 90[C] | 91[D] | 92[C] | 93[C] | 94[C] | 95[C] | 96[C] |
|---|---|---|---|---|---|---|---|---|
| 1 | 39,4 | 36,7 | 35,7 | 36,2 | 37,6 | 38,5 | 38,8 | 38,5 |
| 2 | 35,3 | 27,5 | 27,6 | 27,3 | 27,6 | 27,1 | 26,9 | 26,7 |
| 3 | 217,5 | 76,0 | 73,6 | 75,8 | 75,8 | 78.3 | 78,9 | 76,5 |
| 4 | 47,9 | 39,6 | 39,9 | 39,9 | 40.0 | 38,4 | 38,8 | 42,0 |
| 5 | 54,8 | 48,5 | 48,0 | 48,5 | 48,0 | 55.1 | 55,3 | 49,9 |
| 6 | 18,5 | 18,0 | 18,0 | 18,0 | 18,1 | 18,2 | 18,4 | 18,7 |
| 7 | 33.8 | 32,9 | 32,9 | 32,7 | 33.2 | 32,6 | 32,6 | 32,6 |
| 8 | 39.4 | 36,7 | 36,7 | 37,0 | 37,3 | 39.8 | 39,9[a] | 40,0[a] |
| 9 | 47,1 | 46,8 | 48,0 | 47,9 | 49,0 | 46.8 | 46,8 | 47,0 |
| 10 | 36,6 | 37,0 | 36,8 | 37,0 | 37,1 | 37,2 | 36,9 | 37,0 |
| 11 | 23,0 | 22,6 | 23,6[a] | 22,5[a] | 22,7[a] | 23,4 | 23,6 | 23,7 |
| 12 | 126,0 | 126,8 | 124,8 | 126.8 | 125,5 | 122,2 | 122,6 | 122,7 |
| 13 | 137,8 | 136,1 | 137.5 | 135,8 | 137,5 | 143.4 | 142,8 | 143,0 |
| 14 | 55,9 | 55,6 | 55,3 | 55,5 | 56,1 | 43,7 | 43,7 | 43,9 |
| 15 | 21,2 | 21,8 | 22,7[a] | 21,7[a] | 22.3[a] | 35 5 | 35.8 | 36,2 |
| 16 | 27,5 | 25,3 | 26,2 | 25.2 | 25,3 | 65,9 | 67,7 | 68,0 |
| 17 | 32,9 | 32,7 | 32,9 | 32,7 | 32,9 | 36,8 | 40,0[a] | 40,4[a] |
| 18 | 46,5 | 47,1 | 46,3 | 46,4 | 46,5 | 49.0 | 44,7 | 44,9 |
| 19 | 39,6 | 35,1 | 40,5 | 38.1 | 39,6 | 46,5 | 46,7 | 47.0 |
| 20 | 42,5 | 46,6 | 35 7 | 42,0 | 42,5 | 30.8 | 30,8 | 30,9 |
| 21 | 29,6 | 24,6 | 29,0 | 27,2 | 29,6 | 34,1 | 33,6 | 33,7 |
| 22 | 36.0 | 34,6 | 38,7 | 35,1 | 36,0 | 30,5 | 26,2 | 26,2 |
| 23 | 26,8 | 28,0 | 28,0 | 28,2 | 26,8 | 28,0 | 28,1 | 71,7 |
| 24 | 23,0 | 21 9 | 22,2 | 22.3 | 22,8 | 15,4 | 15,6 | 11,6 |
| 25 | 16,1 | 15,8 | 15,9 | 16,1 | 16.3 | 15,3 | 15,6 | 16,0 |
| 26 | 17,9 | 17,7 | 17,7 | 17,9 | 18,1 | 16,7 | 16.7 | 16,9 |
| 27 | 175,8 | 178,5 | 176,9 | 185,5 | 175,8 | 27,0 | 26,9 | 26,9 |
| 28 | 28,0 | 28,0 | 28,5 | 27,8 | 28,2 | 21 3 | 70,9 | 71,1 |
| 29 | 172,6 | 206,0 | 73,1 | 183,0 | 172.4 | 33,1 | 33.2 | 33,1 |
| 30 | 19,4 | 15,8 | 19,0 | 19,3 | 19,4 | 23.8 | 23.9 | 24,0 |
| OMe |  |  |  |  | 51,6 |  |  |  |

TABLE 13. $^{13}$C NMR Spectra of Compounds (97)-(104)

| C | 97$^{C}$ | 98$^{P}$ | 99$^{C}$ | 100$^{P}$ | 101$^{P}$ | 102$^{P}$ | 103$^{P}$ | 104$^{P}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 38,4 | 38,9 | 38,1 | 41,2 | 44,9 | 44,6 | 46,3 | 38,9 |
| 2 | 26,4 | 28,0 | 26,0 | 84,0 | 71,6 | 71,6 | 71,0 | 27,5 |
| 3 | 76,7 | 78,0 | 71,7 | 81,2 | 73,2 | 75,3 | 75.3 | 77,8 |
| 4 | 41,9 | 39,3 | 55,2 | 54,2 | 42,4 | 46,6 | 54,8 | 38,9[a] |
| 5 | 49,9 | 55,8 | 48,1 | 51,4 | 48,3 | 48,8 | 50,3 | 55,4 |
| 6 | 18,5 | 18,8 | 20,7 | 19 4 | 18,3 | 19,1 | 20.5 | 18,3 |
| 7 | 32,6 | 33,3 | 32,3 | 33.2 | 33,3 | 33,6 | 33,7 | 32,8 |
| 8 | 40,0 | 39,8 | 39,7 | 40,1 | 40,1 | 40,0 | 40,2 | 39,6[a] |
| 9 | 47,0 | 47,2 | 46,7 | 48,1 | 47,7 | 47,9 | 47,5 | 47,0 |
| 10 | 36,9 | 37,3 | 35,9 | 37,6 | 37,3 | 37.1 | 37,5 | 36,8 |
| 11 | 23,4 | 23.7 | 23,2 | 24,6 | 24,0 | 24,1 | 24,3 | 23,4 |
| 12 | 122,6 | 122,4 | 122,2 | 121,9 | 122,6 | 122.7 | 122,9 | 122,5 |
| 13 | 143,1 | 144,9 | 142,8 | 145,1 | 145.1 | 144,4 | 144,6 | 144,0 |
| 14 | 41,6 | 42 0 | 41,4 | 42,7 | 42,3 | 42,0 | 42,4 | 41,4 |
| 15 | 34,7 | 36,0 | 35.4 | 35.8 | 36,1 | 35.9 | 36,1 | 34,3 |
| 16 | 74,9 | 74.6 | 74,7 | 74,2 | 74.8 | 74,3 | 74,5 | 73 3 |
| 17 | 40,6 | 48,8 | 48,7 | 49.0 | 48,9 | 49,1 | 49,6 | 40,0 |
| 18 | 42.8 | 41,3 | 40,5 | 41,2 | 41,5 | 41.3 | 41,7 | 43,2 |
| 19 | 47.0 | 47,3 | 46,4 | 46.9 | 47,2 | 46,9 | 47,2 | 30,2 |
| 20 | 30,4 | 30,9 | 30,3 | 30,8 | 31.0 | 30,8 | 30,8 | 46,7 |
| 21 | 35,4 | 36 0 | 35,4 | 35 8 | 36 1 | 35,9 | 36,1 | 29,5 |
| 22 | 26,8 | 32,7 | 30.3 | 32,4 | 32,8 | 32,3 | 32,1 | 27,5 |
| 23 | 71,9 | 28,7 | 207,0 | 57,8 | 67,8 | 64,3 | 66,5 | 28,3 |
| 24 | 11,5 | 16,5 | 9,0 | 178,7 | 14,6 | 64,7 | 176 9 | 15,4 |
| 25 | 16,1 | 15,6 | 15,7 | 17,8 | 17,4[a] | 17,2 | 16.3 | 16,1[b] |
| 26 | 17,2 | 17,4 | 16,9 | 17,5 | 17,6[a] | 17,3 | 17,3 | 16,6[b] |
| 27 | 27,3 | 27,1 | 27,0 | 27,2 | 27,2 | 27,1 | 27,2 | 27.2 |
| 28 | 70,8 | 179,8 | 177,2 | 177,7 | 180,0 | 177,7 | 177,8 | 69,7 |
| 29 | 32,8 | 33,5 | 32,7 | 33,2 | 33,3 | 33,1 | 33,1 | 23,8 |
| 30 | 25,5 | 24,7 | 24,6 | 24,6 | 24,8 | 24 7 | 25,0 | 207,6 |
| OMe | | | 51,9 | | | | 51.2<br>51,6 | |

TABLE 14. $^{13}$C NMR Spectra of Compounds (105)-(112)

| C | 105$^{C}$ | 106$^{P}$ | 107$^{C}$ | 108$^{C}$ | 109 | 110 | 111 | 112$^{P}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 39.0 | 39,2 | 38,6 | 38,6 | 38,8 | 38.4 | 38,6 | 39,0 |
| 2 | 27.0 | 28,1 | 26,9 | 27,1 | 26,8 | 26.7 | 27.2 | 28,2 |
| 3 | 78,8 | 78,0 | 78,6 | 78,7 | 80,1 | 80,1 | 78,9 | 78,2 |
| 4 | 39,0 | 39.3 | 38,6 | 38,7 | 43,3 | 43,8 | 38,8 | 39,5 |
| 5 | 55,6 | 55.8 | 55.2 | 55,2 | 55.9 | 55.9 | 55,3 | 55,9 |
| 6 | 18,6 | 18,8 | 18,1 | 18,1 | 19,3 | 19,3 | 18,3 | 18,8 |
| 7 | 32,8 | 33,2 | 32,6 | 32.7 | 33.0 | 33,5 | 32,7 | 33,2 |
| 8 | 40,2 | 40,1 | 39,7 | 39,8 | 40,0 | 41,0 | 39,6 | 39,7 |
| 9 | 47.9 | 47,1 | 46,5 | 46,6 | 47,6 | 47,6 | 47,6 | 48,1 |
| 10 | 37,1 | 37,2 | 36,7 | 36,8 | 36,8 | 36,7 | 37,0 | 37,5 |
| 11 | 23,8 | 23,9 | 23,2 | 23.4 | 23,0 | 23.6 | 23,5 | 23,8 |
| 12 | 123,0 | 122,6 | 124,6 | 124.7 | 122.8 | 123,0 | 123,7 | 123,9 |
| 13 | 143,2 | 144.1 | 140,4 | 140.5 | 143,4 | 143,1 | 141,6 | 143,5 |
| 14 | 41,5 | 42,2 | 40.8 | 40,8 | 41,6 | 41,6 | 41,9 | 41,6 |
| 15 | 25.3 | 44,6 | 30,4 | 30,7 | 25,8 | 28,3 | 25,3 | 28,2 |
| 16 | 14,7 | 68,3 | 70,6 | 70,7 | 26,8 | 26,2 | 28,1 | 25,0 |
| 17 | 43,0 | 44,7 | 43.6 | 43,6 | 38,5 | 38,4 | 47,6 | 48 9 |
| 18 | 42,4 | 42,5 | 39,9 | 39,9 | 43,2 | 41,4 | 47,6 | 41,4 |
| 19 | 46,0 | 47,8 | 46,5 | 46,6 | 41,0 | 41,4 | 46,7 | 47,1 |
| 20 | 31,5 | 31,8 | 31,3 | 31,3 | 36,4 | 36,2 | 32,0 | 36.8 |
| 21 | 42,4 | 45,8 | 41,5 | 41,5 | 38,8 | 39,8 | 50,8 | 72,2 |
| 22 | 75,8 | 74,3 | 72,4 | 72,0 | 74.5 | 77,8 | 216,5 | 42,1 |
| 23 | 28.2 | 28,7 | 27,9 | 28,0 | 23,6 | 23,5 | 27,2 | 28,8 |
| 24 | 15,6 | 16,6 | 15.5 | 15,5 | 65.4 | 65,4 | 15,5 | 16,6 |
| 25 | 15,6 | 15.9 | 15,5 | 15,5 | 15,5 | 15,5 | 15,5 | 15,6 |
| 26 | 16,7 | 17.0 | 16.6 | 16,6 | 16,7 | 16,6 | 16,8 | 17,7 |
| 27 | 26,4 | 27,5 | 26.7 | 26,7 | 26,1 | 25,8 | 25,4 | 26,0 |
| 28 | 70,1 | 70,2 | 63,6 | 63,8 | 29,9 | 29,6 | 29,7 | 177,2 |
| 29 | 33,4 | 33,7 | 33.1 | 33,2 | 68,1 | 32.9 | 34.1 | 29,7 |
| 30 | 24,8 | 25,5 | 24 5 | 24.5 | 16,7 | 70,0 | 20.5 | 17,2 |
| OMe | | | | | | | | 51,7 |
| OAc | | | 169,2<br>21,7 | 169.2<br>21,8 | | | | |

TABLE 15. $^{13}C$ NMR Spectra of Compounds (113)-(120)

| C | 113$^{P}$ | 114$^{C}$ | 115$^{C}$ | 116$^{P}$ | 117$^{P}$ | 118$^{P}$ | 119$^{P}$ | 120$^{P}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 38,8 | 38,6 | 39.2 | 39,2 | 39,0 | 38,9 | 39,2 | 38,9 |
| 2 | 27.7 | 27,1 | 27,6 | 28,2 | 28,4 | 28,4 | 23,1 | 28,4 |
| 3 | 73,5 | 77,8 | 78,4 | 78,1 | 80,1 | 80,1 | 78,1 | 80,1 |
| 4 | 42.9 | 38,6 | 39,6 | 39.4 | 43,2 | 43,2 | 39,4 | 43,2 |
| 5 | 48,1 | 55,3 | 56,4 | 55,9 | 56,4 | 56,3 | 55,7 | 55,2 |
| 6 | 18,6 | 18,3 | 18,0 | 18,9 | 19,1 | 19,1 | 18,8 | 19.1 |
| 7 | 32,9 | 32,8 | 30,4 | 33,3 | 33,6 | 33,3 | 32,9 | 33,2 |
| 8 | 39,7 | 39,1 | 40,2 | 40,1 | 40,1 | 40,1 | 40,3 | 40,3 |
| 9 | 48,9 | 47 5 | 48.4 | 48,1 | 48,1 | 48.1 | 48,0 | 48.1 |
| 10 | 37,3 | 36,9 | 38.0 | 37.3 | 37,1 | 37,0 | 37,3 | 37,0 |
| 11 | 23,8 | 23,3 | 24,0 | 23,9 | 24,1 | 24,1 | 23,9 | 24.2 |
| 12 | 123.9 | 122,1 | 121,6 | 122,5 | 122,4 | 122,7 | 122,6 | 122,5 |
| 13 | 143,5 | 143.8 | 143,2 | 144,9 | 144,8 | 144,3 | 144,5 | 144,5 |
| 14 | 41,6 | 41.8 | 42,2 | 42,5 | 42,4 | 41,9 | 42,1 | 42,1 |
| 15 | 28.3 | 27,9 | 35,6 | 26,5 | 26,5 | 26,5 | 26,6 | 26,6 |
| 16 | 24,9 | 26.4 | 74,4 | 28,7 | 28,7 | 28,6 | 27,5 | 27,5 |
| 17 | 48,9 | 46,6 | 51,2 | 38.0 | 38,0 | 35,1 | 39,2 | 39,2 |
| 18 | 41,4 | 41,2 | 40.8 | 45,4 | 45,4 | 47,2 | 44,0 | 44,0 |
| 19 | 47,0 | 40.8 | 47,6 | 46,9 | 46,8 | 46,5 | 47.3 | 47,3 |
| 20 | 36,8 | 35,0 | 30,0 | 30,9 | 30,9 | 36.9 | 36,6 | 36,6 |
| 21 | 72,2 | 72.9 | 79,4 | 42,3 | 42,3 | 72,8 | 74,6 | 74,6 |
| 22 | 42,1 | 39,0 | 37,2 | 75,6 | 75,5 | 47,7 | 79.6 | 79,6 |
| 23 | 68,0 | 28,3 | 28,2 | 28,3 | 23,6 | 23,5 | 28,8 | 23,6 |
| 24 | 13,1 | 15,9[a] | 16,4 | 15,9 | 64,4 | 64,5 | 15,8 | 64,6 |
| 25 | 16,0 | 15,3[a] | 14.3 | 16,6 | 16,3 | 16 2 | 16,5 | 16.2 |
| 26 | 17,7 | 16,8 | 17,2 | 17,3 | 17.1 | 16,9 | 17.1 | 17,0 |
| 27 | 26,0 | 27.6 | 27,6 | 25,8 | 25.7 | 26,0 | 26,7 | 26,7 |
| 28 | 177,2 | 177.6 | 181,0 | 28,8 | 28.7 | 28,7 | 22,3 | 22.3 |
| 29 | 29,7 | 25,3 | 34,0 | 33,3 | 33,3 | 29,9 | 31,5 | 31,5 |
| 30 | 17,3 | 24,8 | 20,5 | 21,2 | 21,1 | 17.7 | 21,3 | 21.3 |
| OMe | 51,7 | 51,2 | | | | | | |

TABLE 16. $^{13}C$ NMR Spectra of Compounds (121)-(128)

| C | 121$^{P}$ | 122$^{P}$ | 123$^{P}$ | 124$^{P}$ | 125$^{P}$ | 126$^{P}$ | 127$^{P}$ | 128$^{P}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 38,9 | 38,9 | 39,0 | 39,4 | 39,3 | 39,2 | 39,3 | 39,1 |
| 2 | 28,4 | 28,4 | 28,5 | 28,7 | 28,2 | 28,1 | 28,2 | 28,1 |
| 3 | 80,1 | 80,1 | 80,2 | 78,0 | 78,1 | 78,1 | 78,1 | 78,0 |
| 4 | 43,2 | 43,2 | 43.2 | 39,4 | 39,3 | 39,4 | 39,4 | 39,3 |
| 5 | 56,3 | 56,2 | 56,4 | 55,6 | 55.6 | 55,8 | 55,7 | 55,8 |
| 6 | 19,1 | 19,1 | 19,2 | 19,1 | 19,1 | 18,8 | 19,2 | 18,8 |
| 7 | 33.2 | 33,1 | 33,6 | 36,4 | 36,8 | 33,3 | 36,8 | 33.2 |
| 8 | 40,3 | 40,3 | 40,1 | 41,1 | 41,5 | 40,1 | 41,5 | 40,1 |
| 9 | 48,1 | 48,0 | 47,3 | 47,3 | 47,3 | 47,2 | 47,5 | 47.1 |
| 10 | 37,0 | 37,0 | 37,0[a] | 37,4[a] | 37,4 | 37 5 | 37,4 | 37,2 |
| 11 | 24,1 | 24.2 | 24,2 | 24.0 | 24,0 | 23.9 | 24,1 | 23.9 |
| 12 | 122,5 | 123,8 | 123,8 | 125,5 | 125,5 | 123.1 | 124,5 | 122,9 |
| 13 | 144,6 | 143,6 | 144,0 | 143,8 | 143,6 | 143,5 | 144,7 | 143,8 |
| 14 | 42,1 | 42,0 | 42,1 | 47.1 | 47,8 | 41,9 | 47.5 | 42.0 |
| 15 | 26,6 | 26,5 | 34,4 | 67,6 | 67.6 | 34,4 | 67,5 | 34,2 |
| 16 | 27,4 | 27,4 | 67,9 | 73,4 | 73,3 | 67,9 | 72,4 | 67,8 |
| 17 | 39,0 | 38,9 | 47,4 | 48,4 | 48,4 | 48,2 | 48,2 | 47,2 |
| 18 | 43,2 | 42,7 | 41.3 | 41,5 | 41,0 | 40,5 | 42 1 | 41,2 |
| 19 | 41,1 | 42.4 | 48,3 | 47,8 | 46.9 | 47,9 | 47,9 | 48.2 |
| 20 | 41,0 | 49,9 | 36,5[a] | 36,8[a] | 36,5 | 36,1 | 36,4 | 36,3 |
| 21 | 70.5 | 70,5 | 78,7 | 78,6 | 79,0 | 82,0 | 78,4 | 78,6 |
| 22 | 79,7 | 79,1 | 77.3 | 73,6 | 73,6 | 73,3 | 77,2 | 77,2 |
| 23 | 23,5 | 23,5 | 23,6 | 28,2 | 28,7 | 28,7 | 28,8 | 28,7 |
| 24 | 64,5 | 64,5 | 64,6 | 16,6[b] | 16,6 | 16,6 | 16,6 | 16,5 |
| 25 | 16.2 | 16,2 | 16,3[b] | 15,9[b] | 16,0 | 15,8 | 16,0 | 15,8 |
| 26 | 17,0 | 16,9 | 16,9[b] | 17,7[b] | 17,6 | 17,0 | 17,7 | 17,0 |
| 27 | 26.7 | 26,5 | 27,3 | 21,2 | 21,1 | 27,4 | 21,1 | 27,4 |
| 28 | 22.3 | 22,1 | 68,4 | 63,2 | 63,1 | 66 2 | 67,8 | 68,4 |
| 29 | 71,7 | 178,7 | 30,6 | 29,5 | 29,5 | 29,8 | 30,6 | 30,5 |
| 30 | 17,5 | 16,5 | 19,5 | 20,2 | 20,1 | 20,4 | 19,4 | 19,4 |

TABLE 17. $^{13}$C NMR Spectra of Compounds (129)-(136)

| C | $129^{\mathrm{DiC}}$ | $130^{\mathrm{P}}$ | $131^{\mathrm{P}}$ | $132^{\mathrm{C}}$ | $133^{\mathrm{C}}$ | $134^{\mathrm{C}}$ | 135 | $136^{\mathrm{C}}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 47,2 | 44,2 | 39,1 | 38,0 | 38,4 | 38.2 | 38,8$^{a}$ | 38,0 |
| 2 | 67,1 | 69,0 | 28,2 | 26 2 | 26,9 | 26,1 | 28,0 | 25,1 |
| 3 | 82,2 | 76.8 | 78,2 | 75,9 | 78,7 | 75,4 | 78,0 | 75.6 |
| 4 | 38,8 | 50,0 | 39,5 | 41,9 | 39,0 | 42.0 | 39,5 | 42,0 |
| 5 | 54,8 | 51,2 | 56,0 | 49,3 | 54,9 | 49.1 | 55,3 | 49 2 |
| 6 | 16,1 | 22,7 | 18,9 | 17,7 | 17,9 | 17,8 | 18,3 | 17.7 |
| 7 | 31,7 | 33,8 | 33,5 | 31,1 | 31,5 | 31,3 | 31,3 | 31.1 |
| 8 | 39.0 | 39.5 | 40,1 | 41,6 | 41,8 | 41,9 | 41,9 | 41.4 |
| 9 | 47,0 | 48.0 | 47,8 | 53,3 | 52,7 | 52,7 | 52,9 | 52,5 |
| 10 | 38.5 | 37,8 | 37,5 | 36,3 | 36,4 | 36,3 | 36,8 | 36.3 |
| 11 | 23,5 | 23,9 | 23,5 | 132,5 | 132,9 | 133,0 | 131,9 | 132.6 |
| 12 | 122,2 | 127,6 | 120,6 | 130,7 | 129,7 | 129,7 | 131,9 | 130,5 |
| 13 | 143,4 | 134,5 | 145.0 | 85,2 | 84.1 | 84,3 | 84,9 | 85,1 |
| 14 | 41,8 | 42,5 | 40.7 | 43,9 | 45,4 | 45,5 | 43.6 | 43,0 |
| 15 | 28,2 | 31,6 | 28,9 | 25,7$^{a}$ | 35,1$^{a}$ | 35,0$^{a}$ | 36.8 | 34,7 |
| 16 | 24,0 | 27,5$^{a}$ | 52 0 | 25,3$^{a}$ | 64,7 | 64,6 | 77,1 | 77,3 |
| 17 | 46,6 | 44,3 | 56,2 | 41,6 | 46,3 | 46,4 | 45.4 | 44,9 |
| 18 | 43,1 | 56,1 | 52,1 | 51,1 | 51,7 | 51,9 | 51,4 | 50,6 |
| 19 | 80,0 | 213,8 | 41,3 | 37,2 | 37,5 | 37,5 | 38,5$^{a}$ | 38,0 |
| 20 | 36.9 | 51,3 | 44,5 | 31,7 | 31.5 | 31,6 | 31,9 | 31.7 |
| 21 | 28,4 | 27,8$^{a}$ | 39,1 | 34,9 | 34,3$^{a}$ | 34,3$^{a}$ | 36,8 | 36,5 |
| 22 | 34,8 | 34,7 | 32,3 | 30,9 | 25,1 | 25,2 | 31,9 | 30,5 |
| 23 | 21,1 | 173 0 | 30,1 | 70,7 | 27.8 | 70,0 | 28,4 | 70,3 |
| 24 | 16,8 | 63,1 | 16,4 | 11,1 | 15,0 | 11,2 | 15,9 | 11,1 |
| 25 | 16,1 | 16,8$^{b}$ | 15,5 | 18,2 | 17,9 | 18,3 | 18,2 | 18,3 |
| 26 | 16,9 | 16,2$^{b}$ | 16,7 | 19,3 | 19.5 | 19,5 | 19,5 | 19,0 |
| 27 | 28.7 | 23,7 | 28,8 | 19,3 | 20,7 | 20,7 | 18,2 | 17,9 |
| 28 | 179,0 | 176,1 | 175,3 | 77,1 | 72,4 | 72,5 | 77,8 | 17,3 |
| 29 | 28,7 | 26,2$^{c}$ | 18,6 | 33.7 | 33,6 | 33,6 | 33,8 | 33,4 |
| 30 | 24,4 | 25,9$^{c}$ |  | 23,6 | 23,7 | 23,8 | 24,4 | 24,2 |
| OMe |  | 52,1 |  |  |  |  |  |  |
| OAc |  | 52,7<br>170,2<br>170,1<br>169,6<br>20,8<br>20,3 |  |  |  |  |  |  |

TABLE 18. $^{13}$C NMR Spectra of Compounds (137)-(144)

| C | $137^{\mathrm{C}}$ | 138 | $139^{\mathrm{P}}$ | $140^{\mathrm{P}}$ | $141^{\mathrm{P}}$ | $142^{\mathrm{M}}$ | $143^{\mathrm{P}}$ | $144^{\mathrm{P}}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 38,2 | 39,0$^{a}$ | 38,4 | 38,8 | 38.4 | 38,2 | 38,5$^{a}$ | 37,9 |
| 2 | 26,2 | 28,1 | 27,6 | 28,1 | 27,6 | 24,4 | 27,9 | 23,4 |
| 3 | 75,2 | 78,0 | 73,3 | 78,5 | 73,1 | 75.6 | 77.9 | 80,6 |
| 4 | 42,2 | 39,5 | 43,0 | 39,6 | 43,1 | 42,4 | 39,4 | 37,9 |
| 5 | 49,0 | 55,4 | 48,4 | 55.7 | 48,2 | 49,3 | 54 3 | 54,8 |
| 6 | 17.8 | 18,9 | 18,7 | 19,0 | 18,6 | 18.6 | 18,6 | 18,1 |
| 7 | 31,2 | 32,6$^{b}$ | 31,9 | 33,1 | 32,4$^{a}$ | 32,3 | 32,8 | 32,1 |
| 8 | 41,8 | 41,1$^{c}$ | 41,0 | 40,7 | 40,5 | 40,0 | 40,3 | 40,0 |
| 9 | 52,8 | 53,9 | 54.0 | 54,6 | 54 5 | 54,6 | 54,0 | 53,4 |
| 10 | 36,4 | 37,0 | 36,8 | 37.3 | 36,8 | 36,8 | 37,0 | 36,6 |
| 11 | 133,2 | 126,2 | 126,3 | 127,1 | 127.1 | 126,4 | 127,5 | 127,6 |
| 12 | 130,3 | 126,2 | 126,3 | 125,8 | 125,7 | 125,8 | 124,9 | 124,5 |
| 13 | 85,5 | 136,1 | 136,0 | 136,7 | 136,4 | 136.8 | 136,6 | 136,6 |
| 14 | 43,8 | 41,9$^{c}$ | 41,9 | 44,6$^{a}$ | 44.4 | 40.5 | 47,3 | 46.9 |
| 15 | 34,3 | 31,9$^{b}$ | 32 8 | 35,1$^{a}$ | 34,8$^{b}$ | 32,3 | 45,7 | 44,7 |
| 16 | 70,5$^{a}$ | 67,7 | 67,6 | 76,5 | 76,5 | 26,3 | 214,7 | 213,9 |
| 17 | 47,5 | 45,3 | 45 4 | 44,8$^{a}$ | 44.4 | 42,6 | 55,0 | 50,8 |
| 18 | 50,4 | 139,1 | 133,0 | 133.7 | 133,3 | 135.1 | 133.4 | 131,2 |
| 19 | 37,4 | 38,6$^{a}$ | 39.2 | 38,7 | 38,4 | 38,5 | 38,2$^{a}$ | 37,9 |
| 20 | 33,2 | 32,6 | 32,8 | 37,8 | 32.7 | 33,1 | 33,4 | 33,5 |
| 21 | 45,7 | 35,5 | 35 4 | 35,4$^{b}$ | 35,1$^{b}$ | 35,3 | 35,2 | 34,9 |
| 22 | 74.3$^{a}$ | 24.5 | 24,4 | 30,2 | 29.9 | 29,2 | 27,4 | 27,2 |
| 23 | 69.6 | 28,5 | 64,7$^{a}$ | 28,5 | 67,4 | 70,0 | 28,5 | 27,8 |
| 24 | 11,3 | 16,0 | 12,6 | 15,8 | 12.6 | 11,4 | 16,0 | 16,2 |
| 25 | 18,4 | 18,4$^{d}$ | 18,6 | 18,3 | 18,6 | 18.5 | 18,1$^{b}$ | 18,0 |
| 26 | 19,1 | 17,3$^{d}$ | 17,5 | 17,2 | 17,1 | 20,6 | 17,2$^{b}$ | 17,0 |
| 27 | 18.1 | 21,9 | 21.9 | 22,1 | 22,0 | 16,8 | 22,1 | 21,8 |
| 28 | 76,9 | 64.7 | 64,4$^{a}$ | 64.1 | 64,0 | 63,6 | 65,8 | 65,9 |
| 29 | 33 2 | 32,6 | 32,5 | 32,3 | 32 3$^{a}$ | 32,5 | 32 2 | 32,5 |
| 30 | 25,2 | 25 1 | 25,1 | 25,0 | 24,8 | 21,5 | 24,0 | 23,8 |

TABLE 19. $^{13}C$ NMR Spectra of Compounds (145)-(149) and (151)-(153)

| C | $145^{C}$ | $146^{C}$ | $147^{P}$ | $148^{P}$ | $149^{C}$ | $151^{C}$ | $152^{C}$ | 153 |
|---|---|---|---|---|---|---|---|---|
| 1 | 41,4 | 38,3 | 37,8 | 37.6 | 37,1 | 37,1 | 37,0[a] | 39,7 |
| 2 | 66,2 | 67,5 | 28,8 | 28.4 | 24,3 | 23.8 | 34,5 | 33,9 |
| 3 | 73,5 | 72,4 | 77,7 | 73.0 | 8 ,6 | 80,1 | 217,3 | 218,3 |
| 4 | 44,0 | 42,0 | 39,6 | 43,2 | 37,9 | 36,9 | 47.2 | 47,1 |
| 5 | 48.4 | 49,7 | 51,8 | 44 6 | 51,2 | 59,9 | 51,7 | 54,8 |
| 6 | 18.3 | 18,0 | 18.7 | 18,5 | 18,2 | 211,9 | 19,1 | 19,6 |
| 7 | 32,6 | 32.4 | 32.5 | 32,2 | 32,1 | 48,5 | 31,2 | 33.9 |
| 8 | 40 9 | 40,8 | 43,1[a] | 43 2 | 38,6[a] | 41,2 | 40,6 | 40,4 |
| 9 | 54,2 | 54,1 | 154,9 | 155.0 | 153.9 | 149,6 | 152.1 | 50,3 |
| 10 | 37,7 | 37,7 | 39,1 | 39,0 | 40,7[a] | 47,6 | 38,1 | 36,8 |
| 11 | 125,7 | 125,4 | 116,1 | 116.1 | 115,9 | 116,6 | 117,3 | 21,4 |
| 12 | 126,2 | 125,9 | 121,2 | 121,2 | 120,7 | 120,9 | 120,4 | 25,9 |
| 13 | 136,3 | 136,0 | 145.4 | 145,4 | 147,2 | 148,9 | 147,2 | 41,3 |
| 14 | 42,1 | 42,0 | 43,3[a] | 43,2 | 42,7 | 42,8 | 42,9 | 42,4 |
| 15 | 32,7 | 32 6 | 36,1 | 36,2 | 25,6 | 25,7 | 27,2 | 29,3 |
| 16 | 21,9 | 24,9 | 66,8 | 66,8 | 27,2 | 27,1 | 25,6 | 33,7[a] |
| 17 | 48,2 | 48,3 | 40.6 | 40,6 | 32,1 | 32,3 | 32,1 | 48,1 |
| 18 | 132,0 | 132,4 | 42,7 | 42,7 | 45,6 | 45,9 | 45.6 | 136,7 |
| 19 | 40.6 | 40.4 | 47,1 | 47,0 | 46 8 | 46.7 | 46,8 | 132,4 |
| 20 | 32,5 | 32.0 | 31,0 | 31,0 | 31,1 | 31,2 | 31,6 | 31,9 |
| 21 | 36,9 | 36,7 | 34,0 | 34,2 | 34,6 | 34,6 | 34,5 | 33.4[a] |
| 22 | 35.5 | 35,4 | 26.1 | 26,1 | 36,9 | 36,9 | 37,7[a] | 33,4[a] |
| 23 | 22.1 | 22,1 | 28,9 | 67,7 | 28,7 | 28,7 | 26,8 | 26,8 |
| 24 | 65.2 | 65,8 | 16,6 | 13.2 | 16,8 | 16,4 | 21.2 | 20.9 |
| 25 | 19,2 | 19,0 | 21.0[b] | 21,1[a] | 20,0[b] | 19,3[a] | 20,5 | 15,8 |
| 26 | 16,2 | 16,1 | 21,3[b] | 21,3[a] | 21,0[b] | 20,8[a] | 19,9 | 16,4 |
| 27 | 19,9 | 19,8 | 25,6 | 26 1 | 28,1 | 27,9 | 25 2 | 14 8 |
| 28 | 177,1 | 176,9 | 69,4 | 69,4 | 25,3 | 25,5 | 28,7 | 176,8 |
| 29 | 24,1 | 24,0 | 33,2 | 33,2 | 33 2 | 33,2 | 33,1 | 30,3 |
| 30 | 32,2 | 32.3 | 24,0 | 24.1 | 23,7 | 23.3 | 23,6 | 29,1 |
| OMe | 51,8 | 51,7 |  |  |  |  |  | 51,8 |
| OAc |  | 171,0<br>170,4<br>170,2<br>21,0<br>20,9 |  |  |  |  |  |  |

TABLE 20. $^{13}C$ NMR Spectra of Compounds (154)-(161)

| C | 154 | $155^{C}$ | $156^{C}$ | $157^{C}$ | $158^{C}$ | $159^{C}$ | $160^{C}$ | $161^{C}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 38,8 | 38,5 | 38,5 | 75,7 | 77,5 | 38,7 | 38,7 | 38,7 |
| 2 | 27,3 | 27,4 | 23,8 | 39,0 | 34 0 | 23,7 | 23,7 | 23,7 |
| 3 | 78,3 | 79,0 | 81,0 | 79,5 | 78,9 | 81,0 | 80,9 | 81,0 |
| 4 | 38,8 | 39,0 | 37.9 | 38,4 | 37,8 | 37 9 | 37,8 | 37,8 |
| 5 | 55,4 | 55,7 | 55,7 | 53.4 | 53,3 | 55,7 | 55,6 | 55,6 |
| 6 | 18,2 | 18,3 | 18.2 | 18,0 | 17.9 | 18,2 | 18,2 | 18.2 |
| 7 | 34,5 | 34,7 | 34,6 | 34,6 | 39.5 | 34,5 | 34,6 | 34,6 |
| 8 | 40,6 | 40,8 | 40,9 | 41,4 | 41,4 | 40,8 | 40,9 | 40,9 |
| 9 | 51,1 | 51,3 | 51,2 | 52,4 | 52,3 | 51,2 | 51,2 | 51,1 |
| 10 | 37,1 | 37,3 | 37 3 | 43,8 | 43,4 | 37,2 | 37,2 | 37,2 |
| 11 | 20,9 | 21,2 | 21 2 | 23,9 | 23,8 | 21,0 | 21,1 | 21,0 |
| 12 | 25,9 | 26,2 | 26,2 | 26,2 | 26,2 | 26,0 | 26,3 | 26,2 |
| 13 | 41,2 | 39.0 | 38,7 | 38,1 | 38,1 | 41,3 | 38,9 | 38,7 |
| 14 | 42,5 | 43,4 | 43,4 | 43,5 | 43,4 | 42,7 | 43,1 | 43,2 |
| 15 | 29,3 | 27.6 | 27,6 | 27,5 | 27,6 | 29.4 | 27,4 | 27,3 |
| 16 | 33,5 | 37.7 | 37,7 | 37,8 | 37,7 | 33,5 | 31,4 | 31,6[a] |
| 17 | 48,1 | 34,4 | 34,4 | 34.4 | 34,3 | 48,0 | 37,9 | 39,6 |
| 18 | 136,9 | 142,8 | 142.7 | 142.7 | 142,6 | 136.7 | 138,2 | 138,7 |
| 19 | 132,3 | 129,8 | 129,8 | 129,7 | 129,7 | 133.1 | 133,7 | 134,4 |
| 20 | 32,0 | 32.3 | 32,4 | 32,4 | 32,3 | 32,1 | 32,2 | 32,3 |
| 21 | 33,5 | 33,4 | 33.4 | 33 5 | 33,4 | 33,5 | 32,9 | 33,3 |
| 22 | 33,5 | 37,4 | 37,5 | 37,5 | 37,4 | 33,5 | 31,4 | 31,4[a] |
| 23 | 27,9 | 28,0 | 28,0 | 28,0 | 27,8 | 28,0 | 27,9 | 27,9 |
| 24 | 16,6 | 15,4 | 16,5 | 15,1 | 16,5 | 16,5 | 16,5 | 16.5 |
| 25 | 15,4 | 16.1 | 16,1 | 12,5 | 12,7 | 16,0 | 16,2 | 16,2 |
| 26 | 15,9 | 16,7 | 16,8 | 16,5 | 16,2 | 16,7 | 16,7 | 16,7 |
| 27 | 14,9 | 14,7 | 14,5 | 14,5 | 14,5 | 14,9 | 14,8 | 14,7 |
| 28 | 176,8 | 25,3 | 25,3 | 25,4 | 25,3 | 182,8 | 65.8 | 65,4 |
| 29 | 30,3 | 31,3 | 31,3 | 31,3 | 31,3 | 30,3 | 30,9 | 30.6 |
| 30 | 29,1 | 29.2 | 29,2 | 29,3 | 29,3 | 29,1 | 29,4 | 29,8 |
| OMe | 51,8 |  |  |  |  |  |  |  |

TABLE 21. $^{13}C$ NMR Spectra of Compounds (162)-(169)

| C | $162^{C}$ | $163^{C}$ | $164^{C}$ | $165^{C}$ | $166^{C}$ | $167^{C}$ | $168^{C}$ | $169^{C}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 38,9 | 39,9 | 38,9 | 39,7 | 41,4 | 40,5 | 39,0 | 38,7 |
| 2 | 22,3 | 34,0 | 34,1 | 33,9 | 27,7 | 23,9 | 27,3 | 23,6 |
| 3 | 88,7 | 217,8 | 216,6 | 217,8 | 78,5 | 80,3 | 78,9 | 80,8 |
| 4 | 38,6 | 47,2 | 47,5 | 47,1 | 39,1 | 38,3 | 38,9 | 37,8 |
| 5 | 56,2 | 55,0 | 55,3 | 54,6 | 55,9 | 55,6 | 56,4 | 56,5 |
| 6 | 18,2 | 19,3 | 19,3 | 19,6 | 18,0 | 17,9 | 18,5 | 18,4 |
| 7 | 34,7 | 34,0 | 33,0[a] | 33,9 | 35,6 | 35,3 | 36,3 | 36,3 |
| 8 | 40,9 | 40,7 | 45,8 | 40,3 | 42,9 | 43,0 | 41,2 | 41,2 |
| 9 | 51,3 | 50,6 | 63,0 | 49,8 | 56,5 | 53,4 | 53,4 | 53,3 |
| 10 | 37,3 | 37,0 | 36,2 | 36,9 | 39,5 | 38,6 | 38,4 | 37,8 |
| 11 | 21,2 | 21,7 | 211,8 | 21,4 | 71,1 | 73,2 | 67,4 | 67,4 |
| 12 | 26,3 | 26,3 | 44,4 | 26,1 | 38,6 | 33,2 | 36,3 | 36,3 |
| 13 | 38,5 | 38,6 | 40,3 | 38,5 | 37,3 | 37,0 | 32,8 | 32,8 |
| 14 | 43,4 | 43,4 | 43,3 | 49,7 | 43,0 | 43,0 | 43,3 | 43,3 |
| 15 | 27,6 | 27,6 | 27,3 | 45,3 | 27,5 | 27,4 | 27,6 | 27,5 |
| 16 | 37,8 | 37,7 | 37,2 | 216,1 | 37,6 | 37,5 | 37,6 | 37,6 |
| 17 | 34,4 | 34,4 | 34,6 | 45,0 | 34,3 | 34,3 | 34,5 | 34,5 |
| 18 | 142,8 | 142,6 | 140,4 | 139,8 | 141,6 | 141,1 | 142,5 | 142,4 |
| 19 | 129,7 | 130,0 | 130,4 | 132,9 | 129,9 | 130,0 | 130,0 | 130,0 |
| 20 | 32,4 | 32,4 | 32,3[a] | 32,2 | 32,4 | 32,4 | 32,4 | 32,4 |
| 21 | 33,4 | 33,4 | 33,1 | 32,6 | 33,4 | 33,3 | 33,3 | 33,3 |
| 22 | 37,4 | 37,4 | 37,2 | 28,0 | 37,3 | 37,3 | 37,4 | 37,4 |
| 23 | 28,0 | 26,9 | 26,2 | 25,8 | 28,2 | 28,2 | 28,2 | 28,1 |
| 24 | 16,2 | 21,0 | 21,5 | 20,9 | 15,6 | 16,6 | 15,5 | 16,5 |
| 25 | 16,7 | 16,0 | 15,9 | 16,3[b] | 17,4 | 17,3 | 20,0[a] | 20,0[a] |
| 26 | 16,2 | 16,0 | 17,4 | 16,5[b] | 16,9 | 17,0 | 18,1[a] | 18,1[a] |
| 27 | 14,6 | 14,5 | 14,2 | 14,9 | 14,3 | 14,2 | 14,7 | 14,6 |
| 28 | 25,3 | 25,3 | 25,1 | 27,0 | 25,3 | 25,2 | 25,2 | 25,1 |
| 29 | 31,4 | 31,3 | 31,1 | 31,2 | 31,3 | 31,3 | 31,3 | 31,3 |
| 30 | 29,3 | 29,2 | 29,1 | 28,7 | 29,2 | 29,1 | 29,2 | 29,2 |
| OMe | 57,5 | | | | | | | |

TABLE 22. $^{13}C$ NMR Spectra of Compounds (170) 177)

| C | $170^{C}$ | $171^{C}$ | $172^{C}$ | $173^{C}$ | $174^{C}$ | 175 | $176^{C}$ | $177^{P}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 159,8 | 56,9 | 38,6 | 38,7 | 38,8 | 38,7 | 38,7 | 38,0 |
| 2 | 125,2 | 63,9 | 23,7 | 23,9 | 27,3 | 27,1 | 26,8 | 28,3 |
| 3 | 205,0 | 212,5 | 80,9 | 80,8 | 78,8 | 78,8 | 74,6 | 78,2 |
| 4 | 44,6 | 44,7 | 37,9 | 37,9 | 38,8 | 38,9 | 42,3 | 39,6 |
| 5 | 53,8 | 45,8[a] | 55,4 | 55,2 | 55,0 | 55,3 | 48,8 | 55,8 |
| 6 | 19,9 | 18,9[b] | 17,7 | 17,7 | 17,7 | 18,4 | 18,3 | 18,3[a] |
| 7 | [illegible] | 33,8 | 34,3 | 34,2 | 34,5 | 32,1 | 31,8 | 32,7 |
| 8 | [illegible] | 41,1 | 42,4[a] | 42,3 | 42,2 | [illegible] | 40,9 | 42,9[b] |
| 9 | 43,2 | 44,1[a] | [illegible] | [illegible] | [illegible] | 49,8 | 49,9 | 47,9 |
| 10 | 41,6 | 38,5 | 36,5 | 36,8 | 36,8 | 36,8 | 36,8 | 37,3 |
| 11 | 21,4 | 22,1 | 28,0 | 19,7 | 19,6 | 38,2 | 38,0 | 19,2[a] |
| 12 | 26,1 | 26,6 | 76,4 | 27,4 | 27,3 | 211,3 | 211,2 | 31,8[c] |
| 13 | 38,6 | 38,5 | 90,7 | 91,8 | 91,7 | 49,3 | 49,4 | 86,1 |
| 14 | 43,5 | 43,4 | 42,2[a] | 42,3 | 42,2 | 44,7[a] | 44,7[a] | 44,6[b] |
| 15 | 27,5 | 27,6 | 27,6 | 26,5 | 26,6 | 35,3 | 35,4 | 34,4 |
| 16 | 37,6 | 37,6 | 21,4 | 20,9 | 20,8 | 65,9 | 65,7 | 73,2[d] |
| 17 | 34,3 | 34,4 | 44,8 | 44,1 | 44,0 | 42,0[a] | 42,0[a] | 46,5 |
| 18 | 142,3 | 142,3 | 51,2 | 50,4 | 50,4 | 39,3 | 39,3 | 50,6 |
| 19 | 129,9 | 130,0 | 39,4 | 37,5 | 37,4 | 32,8 | 32,9 | 36,8 |
| 20 | 32,3 | 32,3[b] | 31,6 | 31,5 | 31,5 | 50,6 | 50,6 | 47,6 |
| 21 | 33,3 | 33,7 | 34,0 | 33,5 | 33,5 | 74,7 | 75,0 | 30,1[c] |
| 22 | 37,4 | 37,4 | 28,9 | 31,4 | 31,4 | 37,1 | 37,0 | 74,1[d] |
| 23 | 27,8 | 27,8 | 28,0 | 28,0 | 28,0 | | 67,4 | 28,8 |
| 24 | 21,4 | 20,8 | 16,5 | 16,5 | 15,2 | 15,4 | 11,6 | 16,6 |
| 25 | 19,0 | 15,8 | 16,5 | 16,1 | 15,9 | 15,3 | 15,8 | 16,4 |
| 26 | 16,7 | 16,6 | 18,7 | 18,3[a] | 18,3[a] | 16,3 | 16,3 | 18,7[a] |
| 27 | 14,7 | 14,4 | 18,7 | 18,4[a] | 18,1[a] | 20,7 | 20,7 | 20,1[a] |
| 28 | 25,3 | 25,3 | 180,1 | 180,3 | 180,3 | 21,3 | 21,4 | 70,3 |
| 29 | 31,3 | 31,3 | 21,0 | 23,7 | 23,8 | 22,3 | 22,5 | 24,2 |
| 30 | 29,2 | 29,3 | 24,0 | 23,7 | 23,8 | 203,7 | 203,7 | 205,3 |
| OAC | | | [illegible]<br>21,4 | 171,0<br>21,3 | | | | 169,8<br>20,9 |

TABLE 23. $^{13}C$ NMR Spectra of Compounds (178)-(185)

| C | 178 P | 179 C | 180 C | 181 C | 182 C | 183 C | 184 C | 185 C |
|---|---|---|---|---|---|---|---|---|
| 1 | 39,1 | 39,8 | 49,9 | 51,1 | 271,3 | 218 6 | 218,9 | 40,5 |
| 2 | 28,3 | 34,0 | 36,5 | 35,8 | 35,4 | 35,8 | 38 6 | 18.7 |
| 3 | 78,0 | 218,0 | 218,0 | 220,8 | 43,0 | 54,3 | 44,2 | 42,1 |
| 4 | 39,5 | 47,3 | 48,1 | 46,4 | 33.3 | 34,0 | 31,9 | 33,3[a] |
| 5 | 55,7 | 54,9 | 57,4 | 52 5 | 57,6 | 59 6 | 59,8 | 56,6 |
| 6 | 18.6[a] | 19,6 | 19,3 | 20,1 | 19,1 | 19,2 | 19,2 | 18,6 |
| 7 | 32,9 | 33,1 | 33 6 | 32,6 | 33,3 | 33.3 | 33,4 | 33,9 |
| 8 | 42,5 | 40,5 | 40 6 | 40.5 | 40,6 | 40,5 | 41,4 | 40,8[b] |
| 9 | 47,8 | 50,4 | 50,6 | 50,5 | 42,2 | 42,3 | 43,3 | 51,1 |
| 10 | 37,3 | 36.9 | 37,5 | 36,8 | 52,6 | 53,2 | 49,7 | 37,5 |
| 11 | 19 3[a] | 21,5 | 21 2 | 22,0 | 23,9 | 24.0 | 23,0 | 20 9 |
| 12 | 31,8 | 26.4 | 26,3 | 26.5 | 25,2 | 26,2[a] | 26 1 | 26,5 |
| 13 | 86.4 | 34,2 | 34,1 | 34,4 | 34 6 | 34,6 | 34.2 | 34,1 |
| 14 | 44,7 | 40,7 | 40.8 | 40,7 | 41,1 | 41,2 | 41,1 | 40,7[b] |
| 15 | 34,6 | 26,4 | 26,4 | 26,4 | 26.4 | 26,4[a] | 26,4[a] | 26,4 |
| 16 | 77,2 | 36,7 | 36,7 | 36,7 | 36,7 | 36,7 | 36,7 | 36,8 |
| 17 | 44,7 | 36,2 | 36.2 | 36,2 | 36,2 | 36,2 | 36,2 | 36.2 |
| 18 | 50,6 | 46.7 | 46 8 | 46,7 | 46.7 | 46.7 | 46,6 | 46,8 |
| 19 | 37,0 | 87.8 | 87,8 | 87,8 | 87,9 | 87,9 | 87,8 | 87,9 |
| 20 | 48.0 | 41,4 | 41,4 | 41 4 | 41.4 | 41,4 | 41,5 | 41,5 |
| 21 | 37,0 | 32,6 | 32,7 | 32,7 | 32,7 | 32,7 | 32,7 | 32,7 |
| 22 | 33.8 | 26 2 | 26.2 | 26,2 | 26,3 | 26,3[a] | 26,3[a] | 26,3 |
| 23 | 28 7 | 26,7 | 27,2 | 29,4 | 31,9 | 32,1 | 31.1 | 33,4[a] |
| 24 | 16.6 | 21,0 | 21,8 | 19.5 | 22,7 | 22,3 | 25,9 | 21,5 |
| 25 | 16,6 | 16,3 | 16,4 | 15.5 | 15.7 | 16,0[b] | 15,9[b] | 16.4 |
| 26 | 18,2 | 15.5 | 15.8 | 15,1 | 16.4 | 16,5[b] | 16,6[b] | 15,8 |
| 27 | 19,6 | 13,4 | 13,4 | 13,4 | 13,4 | 13,4 | 13.2 | 13.5 |
| 28 | 78,0 | 71,2 | 71,2 | 71,2 | 71,3 | 71,3 | 71,3 | 71.3 |
| 29 | 24,8 | 24,5 | 24,5 | 24,5 | 24.5 | 24,5 | 24,5 | 24,5 |
| 30 | 207,2 | 28,8 | 28,8 | 28,8 | 28,8 | 28,8 | 28,8 | 28,8 |
| 31 |  |  | 15,6 | 18,8 |  | 15,1 | 15,9 |  |

TABLE 24. $^{13}C$ NMR Spectra of Compounds (186)-(188)

| C | 186 C | 187 C | 188 C | C | 186 C | 187 C | 188 C |
|---|---|---|---|---|---|---|---|
| 1 | 45.1 | 38.9 | 48,6 | 18 | 46,8 | 46,8 | 46,8 |
| 2 | 26.0 | 27.4 | 30,6 | 19 | 87,9 | 87,9 | 87,9 |
| 3 | 49,9 | 78,9 | 84 7 | 20 | 41,5 | 41,5 | 41.5 |
| 4 | 32,4 | 38.9 | 39,0 | 21 | 32,7 | 32,7 | 32,7 |
| 5 | 51.6[a] | 55,5 | 55,8 | 22 | 26,3 | 26,3 | 26,3 |
| 6 | 18 8 | 18,2 | 18,5 | 23 | 31,0 | 28.0 | 28,4 |
| 7 | 33,2 | 33,9 | 33,9 | 24 | 22,2[c] | 15,4 | 16,2 |
| 8 | 40,9[b] | 40,6[a] | 40,6[a] | 25 | 24,8 | 16,5 | 17,3 |
| 9 | 50,0[a] | 51,1 | 51,0 | 26 | 15,4 | 15,7 | 15,7 |
| 10 | 38,0 | 37.2 | 37,5 | 27 | 13 4 | 13,5 | 13,5 |
| 11 | 21,8 | 21,0 | 21,0 | 28 | 71,3 | 71,2 | 71,2 |
| 12 | 26,7 | 26,4 | 26.4 | 29 | 24,5 | 24,5 | 24,5 |
| 13 | 34,5 | 34,1 | 34,1 | 30 | 28.8 | 28,8 | 28,8 |
| 14 | 40,7[b] | 40 7[a] | 40,7[a] | 31 | 28,2[c] |  | 19.4 |
| 15 | 26.4 | 26,4 | 26,4 |  |  |  |  |
| 16 | 36,8 | 36,7 | 36,7 |  |  |  |  |
| 17 | 36,2 | 36,2 | 36,2 |  |  |  |  |

Budesinsky and Klinot [56] used $^{13}C$ NMR spectroscopy to evaluate the contribution of conformational states to the total conformation of ring A in the triterpenoid ketones of the oleanane series (179), (182). Assuming that in the 2β-methyl-3-ketone (181) ring A is present in the boat form, and in the 2α-methyl-3-ketone (180) in the chair form, these authors showed that in the case of the unsubstituted 3-ketone (179) the contribution of the boat form amounted to from 50 to 33%. For the 1-ketone (182), this contribution ranged from 8 to 31%. They also discussed the values of the relaxation times for the carbon atoms of the compounds that they studied. In all cases, the quaternary carbon atoms have long relaxation times ($T_1 \geq 5$ sec) which permits them to be readily distinguished from the methylene carbon atoms ($T_1 = 0.3$-$0.8$ sec). The values of $T_1$ for the methine carbon atoms were close to 1 sec, while for the methyl group they depended on their positions in the triterpene skeleton. Thus, the values of $T_1$ for the geminal C-29 and C-30 methyl groups (0.5 and 0.6 sec) were appreciably shorter than those for the skeletal methyl groups involving C-25 (0.9 sec), C-26 (4.1 sec), and C-27 (4.5 sec). Of the pairs of methyl groups at C-4, $T_1$ for

TABLE 25. Values of the Glycosylation Shifts of Compounds (4), (6), (15-17), (19), and (100-103)

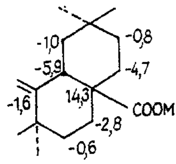
| Initial compounds | Carbohydrate chain | Positions of attachment of the carbohydrate chains and glycosylation shifts | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 10 | 25 | 23 | 24 |
| $4^{P*}$[8] | β-*D*-Glc | | | −1,2 | | | | | | +7,2 | |
| $4^{P*}$[9] | β-*D*-Glc | | −1,7 | +8,5 | +0,6 | | | | | −3.1 | +0,6 |
| 6 [8] | α-*L*-Ara | | | +8,6 | +1,1 | | | −0,5 | −0,6 | | −1.2 |
| 15 [9] | β-*D*-Glc | | −1 7 | +10.4 | +1,1 | −0,5 | | | | −2,4 | +0,5 |
| 16 [15] | α-*L*-Ara$^2$-β-*D*-Glc | −0,8 | −0.9 | +9,5 | | | | | | −3,0 | |
| 17 [14] | β-*D*-Glc | | −1,7 | +11,8 | | +0,5 | | | | −0,5 | +0,8 |
| 19 [9] | β-*D*-Glc | | −0,8 | +10,1 | | | | | | | +1,6 |
| 100 [30] | β-*D*-Glc | | −1,2 | +8,6 | | +0,6 | | | | | −1,1 |
| 101 [30] | β-*D*-Glc | −0,8 | −1,3 | +9,7 | +0,5 | −0,8 | | | | −2,8 | +0,6 |
| 102 [30] | β-*D*-Glc | | −2 3 | +11,1 | +1,1 | −0,8 | +0,5 | | | −0 5 | +1,6 |
| 103 [30] | β-*D*-Glc | −0,5 | −1,2 | +9,1 | +1,4 | | | | −0,6 | −2,1 | −1,4 |

*The letter P above a compound number means that the spectrum of the aglycon was taken in pyridine-$d_5$.

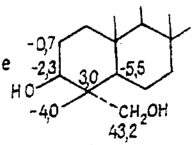
TABLE 26. Values of the Glycosylation Shifts of Compounds (106) and (123)

| Initial compound | Carbohydrate chain | Positions of attachment of the carbohydrate chains and glycosylation shifts | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 16 | 17 | 18 | 20 | 21 | 22 | 28 | 29 | 30 |
| 106 [32] | β-*D*-Glc- | +0,8 | +0,5 | | | | −1 0 | +6.8 | | |
| 123 [38] | β-*D*-Fac- | | +0.5 | −0,7 | +0,5 | +13,5 | −3,3 | −4,0 | 0,6 | +0,9 |

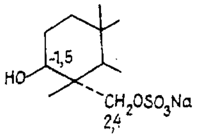
C-23 group (~0.5 sec) was only half that for the C-24 methyl group (~1 sec). These observations in general agree with literature figures for friedelin [57].



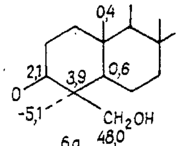
2a
1→2



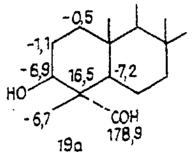
4a
2→4



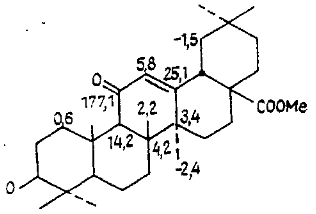
4b [7]



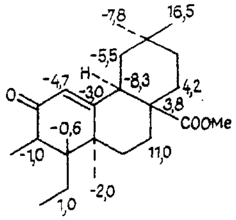
$^{P}$6a
2→6



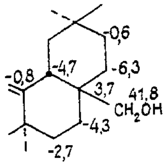
19a
2→19



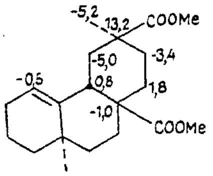
21a
2→21



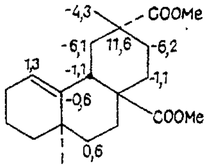
23a
20→23



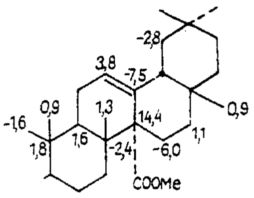
27a
1→27



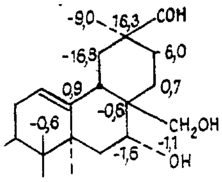
33a
8→33



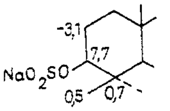
34a 2→34



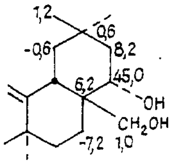
87a
1 → 87



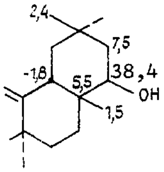
104a
97 → 104



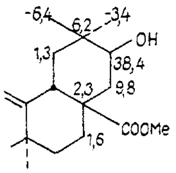
98a [29]



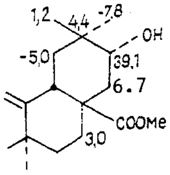
105a
27 → 105



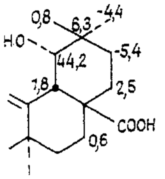
116a P
1 → 116



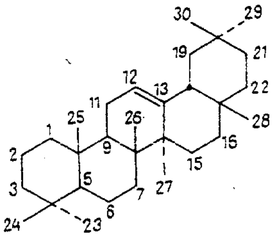
112a
2 → 112$^n$



114a
2 → 114



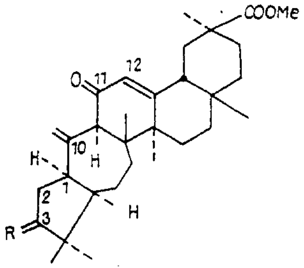
129a
2 → 129



1. [1] $\Delta^{12(13)}$, 3β-OH, β-amyrin
2. $\Delta^{12(13)}$, 3β-OH, 17-COOMe. Oleanolic acid (M.E.)
3. $\Delta^{12(13)}$, 3- =0, 17-COOMe. 3-Oxcolean-12-en-28-oic acid (M.E.
4. $\Delta^{12(13)}$, 3β-OH, 4α-$CH_2OH$, 17-COOMe. Hederagenin (M.E.)
5. [10] $\Delta^{12(13)}$, 3- =0, 4α-$CH_2OH$, 17-COOMe. 23-Hydroxy-3-oxoolean-12-en-28-oic acid (M.E.)
6. [8] $\Delta^{12(13)}$, 3β-OH, 4β-$CH_2OH$, 17-COOH. 4-Epihederagenin
7. [10] $\Delta^{12(13)}$, 3- =0, 4β-$CH_2OH$, 17-COOMe. 24-Hydroxy-3-oxoolean-12-en-28-oic acid (M.E.)
8. [11] $\Delta^{12(13)}$, 3α-OH, 4β-$CH_2OH$, 17-COOMe. 3α,24-Dihydroxyolean-12-en-28-oic acid (M.E.)
9. $\Delta^{12(13)}$, 3α-OH, 4β-$CH_2OAc$, 17-COOMe. 24-Acetoxy-3α-hydroxyolean-12-en-28-oic acid (M.E.)
10. $\Delta^{12(13)}$, 3α-OAc, 4β-$CH_2OAc$, 17-COOMe. 3α,24-Diacetoxyolean-12-en-28-oic acid (M.E.)
11. [12] $\Delta^{12(13),20(30)}$, 3β-OH, 17-COOMe. Akebonaic acid (M.E.)
12. $\Delta^{12(13),20(30)}$, 3α-OH, 17-COOMe. 3-Epiakebonoic acid (M.E.)
13. [13] $\Delta^{12(13)}$, 2α-OH, 3α-OH, 4β-$CH_2OH$, 17-COOMe. 2α,3α,24-Trihydroxyolean-12-en-28-oic acid (M.E.)
14. $\Delta^{12(13)}$, 2α-OAc, 3α-OAc, 4β-$CH_2OAc$, 17-COOMe. 2α,3α,24-Triacetoxyolean-12-en-28-oic acid (M.E.)
15. [14] $\Delta^{12(13)}$, 2α-OH, 3β-OH, 4α-$CH_2OH$, 17-COOH. Arjunolic acid
16. [15] $\Delta^{12(13)}$, 2β-OH, 3β-OH, 4α-$CH_2OH$, 17-COOH. Bayogenin
17. [1] $\Delta^{12(13)}$, 2α-OH, 3β-OH, 17-COOMe. Maslinic acid (M.E.)
18. $\Delta^{12(13)}$, 2α-OH, 3α-OH, 17-COOMe. 3-Epimaslinic acid (M.E.)
19. $\Delta^{12(13)}$, 3β-OH, 4α-COH, 17-COOMe. Gypsogenin
20. [16] $\Delta^{12(13)}$, 3β-OAc, 11- =0, 7-COOMe. 3-O-Acetyl-11-oxo-18β-oleanolic acid (M.E.)

21. $\Delta^{12(13)}$, 3β-OH, 11- =0, 17-COOMe. 11-Oxo-18β-oleanolic acid (M.I
22. $\Delta^{12(13)}$, 3- =0, 11- =0, 17-COOMe. 3,11-Dioxo-18β-olean-12-en-28-oic acid (M.E.)
23. $\Delta^{12(13)}$, 3β-OAc, 11- =0, 17-COOMe, 18α-H. 3-O-Acetyl-11-oxo-18α-oleanolic acid (M.E.)
24. $\Delta^{12(13)}$, 3β-OH, 11- =0, 17-COOMe, 18α-H. 11-Oxo-18α-oleanolic acid (M.E.)
25. $\Delta^{12(13)}$, 3- =0, 11- =0, 17-COOMe, 18α-H. 3,11-Dioxo-18α-olean-12-en-28-oic acid (M.E.)
26. [17] $\Delta^{12(13)}$, 3β-OAc, 11- =0, 3-O-Acetyl-11-oxo-β-amyrin.
27. [1] $\Delta^{12(13)}$, 3β-OH, 4α-$CH_2OH$, 17-$CH_2OH$. 23-Oxoerythrodiol
28. [24] $\Delta^{12(13)}$, 3β-OH, 4α-COOH, 17-COOH. Gypsogenic acid
29. [12] $\Delta^{12(13)}$, 3β-OH, 17-COOMe, 20α-$CH_2OH$. Mesembryanthemoidigenic acid (M.E.)
30. $\Delta^{12(13)}$, 3β-OH, 17-COOMe, 20β-$CH_2OH$. Queretaroic acid (M.E.)
31. [18] $\Delta^{12(13)}$, 3- =0, 17-$CH_2OAc$, 20α-$CH_2OAc$. 28,29-Diacetoxy-3-oxoolean-12-ene
32. $\Delta^{12(13)}$, 3β-OAc, 17-$CH_2OAc$, 20β-$CH_2OAc$. Queretarol triacetate
33. [11] $\Delta^{12(13)}$, 3α-OH, 4β-$CH_2OH$, 17-COOMe, 20β-COOMe. 3α-24-Dihydroxyolean-12-ene-28,30-dioic acid (di-M.E.)
34. [19] $\Delta^{12(13)}$, 3β-OH, 17-COOMe, 20α-COOMe. Serratagenic acid (di-M.E.)
35. [61] $\Delta^{12(13)}$, 2β-OH, 3β-OAc, 4α-$CH_2OH$, 17-COOH, 20β-COOMe. Phytolaccagenin A
36. $\Delta^{12(13)}$, 2β-OH, 3β-OH, 17-COOMe, 20β-COOH. Acinosolic acid
37. $\Delta^{12(13)}$, 2β-OH, 3β-OAc, 4α-$CH_2OH$, 17-COOMe, 20β-COOMe. Phytolaccagenin A (M.E.)
38. $\Delta^{12(13)}$, 2β-OAc, 3β-OAc, 4α-$CH_2OAc$, 17-COOH, 20β-COOMe. 2,23-Di-O-acetylphytolaccagenin A
39. $\Delta^{12(13)}$, 2β-OAc, 3β-OAc, 17-COOMe, 20β-COOH. 2,3-Di-O-acetylacinosolic acid
40. $\Delta^{12(13)}$, 2β-OAc, 3β-OAc, 4α-$CH_2OAc$, 17-COOMe, 20β-COOH. 2β,3β-23-Triacetoxyolean-12-ene-28,30-dioic acid (28-M.E.)
41. $\Delta^{12(13)}$, 3β-OAc, 4α-$CH_2OAc$, 17-COOMe, 20β-COOH. Diacetoxyolean-12-en-28,30-dioic acid (28-M.E.)
42. $\Delta^{12(13)}$, 3β-OH, 17-COOH, 20β-COOMe. 3β-Hydroxyolean-12-en-28,30-dioic acid (30-M.E.)
43. $\Delta^{12(13)}$, 3β-OAc, 17-COOH, 20β-COOMe. 3β-Acetoxyolean-12-en-28,30-dioic acid (30-M.E.)
44. [19] $\Delta^{12(13)}$, 2β-OH, 3β-OH, 4α-$CH_2OH$, 17-COOH, 20β-COOMe. Phytolaccagenin
45. [21] $\Delta^{12(13)}$, 3β-OAc, 11- =0, 20β-COOMe. 3-O-Acetylglycyrrhetic acid (M.E.)
46. [20] $\Delta^{12(13)}$, 3β-OAc, 11- =0, 20α-COOMe. 3-O-Acetylliquiritic acid (M.E.)
47. $\Delta^{12(13)}$, 3β-OAc, 20β-COOMe. 3β-Acetoxyolean-12-en-30-oic acid (M.E.)
48. $\Delta^{12(13)}$, 3β-OAc, 20α-COOMe. 3β-Acetoxyolean-12-en-29-oic acid (M.E.)
49. [21] $\Delta^{12(13)}$, 3β-OH, 11- =0, 20β-COOMe. Glycyrrhetic acid (M.E.)
50. $\Delta^{12(13)}$, 3- =0, 11- =0, 20β-COOMe. 3,11-Dioxoolean-12-en-30-oic acid (M.E.)
51. $\Delta^{12(13)}$, 3β-OH, 20β-COOMe. 3β-Hydroxyolean-12-en-30-oic acid (M.E.)
52. $\Delta^{12(13)}$, 3β-OH, 20β-$CH_2OH$. 3β,30-Dihydroxyolean-12-ene
53. $\Delta^{12(13)}$, 3β-OAc, 20β-$CH_2OAc$. 3β,30-Diacetoxyolean-12-ene
54. $\Delta^{12(13)}$, 3β-OAc, 11- =0, 20β-COOMe, 18α-H. 3-O-Acetyl-18α-glycyrrhetic acid (M.E.)
55. [20] $\Delta^{12(13)}$, 3β-OAc, 11- =0, 20α-COOMe, 18α-H. 3-O-Acetyl-18α-liquiritic acid (M.E.)
56. [21] $\Delta^{12(13)}$, 3β-OH, 11- =0, 20β-COOMe, 18α-H. 18α-Glycyrrhetic acid (M.E.)
57. $\Delta^{12(13)}$, 3- =0, 11- =0, 20β-COOMe, 18α-H. 3,11-Dioxo-18α-olean-12-en-30-oic acid (M.E.)
58. $\Delta^{12(13)}$, 3β-OH, 20β-COOMe, 18α-H. 3β-Hydroxy-18α-olean-12-en-30-oic acid (M.E.)
59. $\Delta^{12(13)}$, 3β-OH, 20β-$CH_2OH$, 18α-H. 3β,30-Dihydroxy-18α-olean-12-ene
60. $\Delta^{12(13)}$, 3β-OAc, 20β-$CH_2OAc$, 18α-H. 3β,30-Diacetoxy-18α-olean-12-ene
61. [22] $\Delta^{12(13)}$, 3β-OAc, 11- =0, 20β-COCl
62. $\Delta^{12(13)}$, 3β-OAc, 11- =0, 20β-NCO
63. $\Delta^{12(13)}$, 3β-OAc, 11- =0, 20β-NHCOOMe
64. $\Delta^{12(13)}$, 3β-OAc, 11- =0, 20β-NHCONHPh
65. $\Delta^{12(13)}$, 3β-OAc, 11-OAc, 20β-$CH_2OAc$. 3β,11,30-Triacetoxyolean-12-ene
66. $\Delta^{12(13)}$, 11- =0, 20β-COOMe. 11-Oxoolean-12-en-30-oic acid (M.E.)
67. $\Delta^{13(18)}$, 3β-OAc, 11- =0, 20β-COOMe. 3β-Acetoxy-11-oxoolean-13(18)-en-30-oic acid (M.E.)

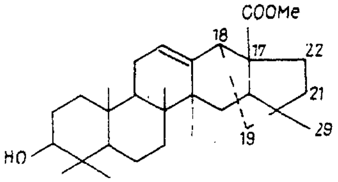
68. [23] $\Delta^{9(11),13(18)}$, 3β-OAc, 12- =O, 19- =O, 20α-COOMe. 3β-Acetoxy-12,19-dioxoolean-9(11),13(18)-dien-29-oic acid (M.E.)
69. $\Delta^{9(11),13(18)}$, 3β-OAc, 12- =O, 19- =O, 20β-COOMe. 3β-Acetoxy-12,19-dioxoolean-9(11),13(18)-dien-30-oic acid (M.E.)
70. $\Delta^{9(11)}$, 3β-OAc, 20β-COOMe. 3β-Acetoxyolean-9(11)-en-30-oic acid (M.E.)
71. $\Delta^{9(11)}$, 3β-OAc, 12- =O, 20β-COOMe. 3β-Acetoxy-12-oxoolean-9(11)-en-30-oic acid (M.E.)
72. [62] $\Delta^{12(13)}$, 1α-OH, 3β-OH, 20α-COOH. Imberbic acid
73. $\Delta^{12(13)}$, 1α-OAc, 3β-OAc, 20α-COOH. 1,3-Di-O-acetylimberbic acid
74. $\Delta^{12(13)}$, 1α-OAc, 3β-OAc, 20α-COOMe. 1,3-Di-O-acetylimberbic acid (M.E.)
75. $\Delta^{12(13)}$, 1- =O, 3- =O, 20α-COOH. 1,3-Dioxoolean-12-en-20-oic acid



76. [25] R = H, β-OH
77. R = H, β-OAc
78. R = O

79. [26] $\Delta^{12(13)}$, 3β-OH, 6α-OH, 14-COOMe. Manevalic acid (M.E.)
80. $\Delta^{12(13)}$, 3β-OH, 6α-OH, 14-COOMe, 17-COOMe. Azizic acid (di-M.E.)
81. [27] $\Delta^{12(13)}$, 3α-OH, 14-COOH. 3α-Hydroxyolean-12-en-27-oic acid
82. $\Delta^{12(13)}$, 3α-OH, 14-COOMe. 3α-Hydroxyolean-12-en-27-oic acid (M.E.)
83. $\Delta^{12(13)}$, 3α-OAc, 14-COOH. 3α-Acetoxyolean-12-en-27-oic acid
84. $\Delta^{12(13)}$, 3α-OAc, 14-COOMe. 3α-Acetoxyolean-12-en-27-oic acid (M.E.)
85. $\Delta^{12(13)}$, 3- =O, 14-COOH. 3-Oxoolean-12-en-27-oic acid
86. $\Delta^{12(13)}$, 3- =O, 14-COOMe. 3-Oxoolean-12-en-27-oic acid (M.E.)
87. $\Delta^{12(13)}$, 3β-OH, 14-COOMe. 3β-Hydroxyolean-12-en-27-oic acid (M.E.)
88. $\Delta^{12(13)}$, 3- =O, 14-COOH, 20α-CHO. 3,29-Dioxoolean-12-en-27-oic acid
89. $\Delta^{12(13)}$, 3- =O, 14-COOMe, 20α-COOMe. 3-Oxoolean-12-ene-27,29-dioic acid (di-M.E.)
90. $\Delta^{12(13)}$, 3α-OH, 14-COOH, 20α-CHO. 3α-Hydroxy-29-oxoolean-12-en-27-oic acid
91. $\Delta^{12(13)}$, 3α-OH, 14-COOH, 20α-$CH_2OH$. 3α-29-Dihydroxyolean-12-en-27-oic acid
92. $\Delta^{12(13)}$, 3α-OH, 14-COOH, 20α-COOH. 20α-Hydroxyolean-12-ene-27,29-dioic acid
93. $\Delta^{12(13)}$, 3α-OH, 14-COOMe, 20α-COOMe. 3α-Hydroxyolean-12-ene-27,29-dioic acid (di-M.E.)
94. [28] $\Delta^{12(13)}$, 3β-OH, 16β-OH. 16β-Hydroxy-β-amyrin
95. [1] $\Delta^{12(13)}$, 3β-OH, 16β-OH, 17-$CH_2OH$. Longispinogenin
96. $\Delta^{12(13)}$, 3β-OH, 4α-$CH_2OH$, 16β-OH, 17-$CH_2OH$. 23-Hydroxylongispinogenin
97. $\Delta^{12(13)}$, 3β-OH, 4α-$CH_2OH$, 16α-OH, 17-$CH_2OH$. 23-Hydroxyprimulagenin A
98. [29] $\Delta^{12(13)}$, 3β-OH, 16α-OH, 17-COOH. Echinocystic acid
99. [1] $\Delta^{12(13)}$, 3β-OH, 4α-CHO, 16α-OH, 17-COOMe. Quillaic acid (M.E.)
100. [30] $\Delta^{12(13)}$, 3β-OH, 2β-O-CO-4β, 4α-$CH_2OH$, 16α-OH, 17-COOMe. Platycogenic acid A lactone
101. [15] $\Delta^{12(13)}$, 2β-OH, 3β-OH, 4α-$CH_2OH$, 16α-OH, 17-COOH. Polygalacic acid
102. [30] $\Delta^{12(13)}$, 2β-OH, 3β-OH, 4α-$CH_2OH$, 4β-$CH_2OH$, 16α-OH, 17-COOMe. Platycogenin
103. $\Delta^{12(13)}$, 2β-OH, 2β-OH, 4α-$CH_2OH$, 4β-COOMe, 16α-OH, 17-COOMe. Platycogenic acid A (M.E.)
104. [31] $\Delta^{12(13)}$, 3β-OH, 16α-OH, 17-$CH_2OH$, 20β-CHO. Cyclamiretin
105. [1] $\Delta^{12(13)}$, 3β-OH, 17-$CH_2OH$, 22α-OH. 22α-Hydroxyerythrodiol
106. [32] $\Delta^{12(13)}$, 3β-OH, 16α-OH, 17-$CH_2OH$, 22α-OH. Camelliagenin A
107. $\Delta^{12(13)}$, 3β-OH, 16α-OAc, 17-$CH_2OH$, 22α-OCO($CH_3$)C=CH($CH_3$)-trans. 16-O-Acetyl-22-O-angeloylcamelliagenin A
108. $\Delta^{12(13)}$, 3β-OH, 16α-OAc, 17-$CH_2OH$, 22α-OCOCH($CH_3$)$CH_2CH_3$. 16-O-Acetyl-22-O-(2'-methylbutyroyl)-camelliagenin
109. [33] $\Delta^{12(13)}$, 3β-OAc, 4β-$CH_2OAc$, 20α-$CH_2OAc$, 22β-OAc. 3,24,29,22-Tetra-O-acetylabrisapogenol B
110. $\Delta^{12(13)}$, 3β-OAc, 4β-$CH_2OAc$, 20β-$CH_2OAc$, 22β-OAc. 3,24,30,22-Tetra-O-acetylabrisapogenol E

111. $\Delta^{12(13)}$, 3β-OH, 22- =O. Abrisapogenol F
112. [14] $\Delta^{12(13)}$, 3β-OH, 17-COOMe, 21β-OH. 21β-Hydroxyoleanolic acid (M.E.)
113. $\Delta^{12(13)}$, 3β-OH, 4α-$CH_2OH$, 17-COOMe, 21β-OH. 21β-Hydroxyhederagenin (M.E.)
114. [34] $\Delta^{12(13)}$, 3β-OH, 17-COOMe, 21α-OH. 21α-Hydroxyoleanolic acid (M.E.)
115. [35] $\Delta^{12(13)}$, 3β-OH, 16α-OH, 17-COOH, 21β-$OCOC_9H_{13}O$. Acacigenin B
116. [36] $\Delta^{12(13)}$, 3β-OH, 22β-OH. Sophoradiol
117. $\Delta^{12(13)}$, 3β-OH, 4β-$CH_2OH$, 22β-OH. Soyasapogenol B
118. $\Delta^{12(13)}$, 3β-OH, 4β-$CH_2OH$, 21β-OH. Kudzusapogenol C
119. $\Delta^{12(13)}$, 3β-OH, 21β-OH, 22β-OH. Cantoniensistriol
120. $\Delta^{12(13)}$, 3β-OH, 4β-$CH_2OH$, 21β-OH, 22β-OH. Soyasapogenol A
121. $\Delta^{12(13)}$, 3β-OH, 4β-$CH_2OH$, 20α-COOMe, 21β-OH, 22β-OH. Kudzusapogenol A
122. $\Delta^{12(13)}$, 3β-OH, 4β-$CH_2OH$, 20α-COOMe, 21β-OH, 22β-OH. Kudzusapogenol B (M.E.)
123. [38] $\Delta^{12(13)}$, 3β-OH, 4β-$CH_2OH$, 16α-OH, 17-$CH_2OH$, 21β-OH, 22α-OH. Protoaescigenin
124. $\Delta^{12(13)}$, 3β-OH, 15α-OH, 16α-OH, 17-$CH_2OH$, 21β-OCO($CH_3$C=CH($CH_3$)-trans, 22α-OCO($CH_3$)C=CH($CH_3$). 21,22-Diangeloyl-$R_1$-barrigenol
125. [39] $\Delta^{12(13)}$, 3β-OH, 15α-OH, 16α-OH, 17-$CH_2OH$, 21β-OCO($CH_3$)C=CH($CH_3$), 22α-OCO($CH_3$)·C=C($CH_3$)H-cis. 21-O-angeloyl-22-O-tigloyl-$R_1$-barrigenol
126. $\Delta^{12(13)}$, 3β-OH, 16α-OH, 17-$CH_2OH$, 21β-OCO($CH_3$)C=CH($CH_3$), 22α-OH. 21-O-Angeloylbarringtogenol C
127. $\Delta^{12(13)}$, 3β-OH, 15α-OH, 16α-OH, 17-$CH_2OH$, 21β-OH, 22α-OH. $R_1$-Barrigenol
128. $\Delta^{12(13)}$, 3β-OH, 16α-OH, 17-$CH_2OH$, 21β-OH, 22α-OH. Barringtogenol C
129. [40] $\Delta^{12(13)}$, 2α-OH, 3β-OH, 17-COOH, 19α-OH. Arjunic acid
130. [41] $\Delta^{12(13)}$, 2α-OAc, 3β-OAc, 4α-COOMe, 4β-$CH_2OAc$, 17-COOMe, 19- =O. 2α,3β,24-Triacetoxy-19-oxoolean-12-ene-23,28-dioic acid (di-M.E.)



131. [42] Pfaffic acid (M.E.)
132. [1] $\Delta^{11(12)}$, 3β-OH, 4α-$CH_2OH$, 13β-$OCH_2$-17. 16-Deoxysaikogenin
133. $\Delta^{11(12)}$, 3β-OH, 16β-OH, 13β-$OCH_2$-17. Saikogenin E
134. $\Delta^{11(12)}$, 3β-OH, 4α-$CH_2OH$, 16β-OH, 13β-$OCH_2$-17. Saikogenin F
135. [43] $\Delta^{11(12)}$, 3β-OH, 16α-OH, 13β-$OCH_2$-17. Rotundiogenin A
136. [1] $\Delta^{11(12)}$, 3β-OH, 4α-$CH_2OH$, 16α-OH, 13β-$OCH_2$-17. Saikogenin G
137. $\Delta^{11(12)}$, 3β-OH, 4α-$CH_2OH$, 16α-OH, 13β-$OCH_2$-17, 22α-OH. 22α-Hydroxysaikogenin
138. [43] $\Delta^{11(12),13(18)}$, 3β-OH, 16α-OH, 17-$CH_2OH$. 16-Episaikogenin C
139. [44] $\Delta^{11(12),13(18)}$, 3β-OH, 4α-$CH_2OH$, 16α-OH, 17-$CH_2OH$. Saikogenin D
140. $\Delta^{11(12),13(18)}$, 3β-OH, 16β-OH, 17-$CH_2OH$. Saikogenin C
141. $\Delta^{11(12),13(18)}$, 3β-OH, 4α-$CH_2OH$, 16β-OH, 17-$CH_2OH$. Saikogenin A
142. [45] $\Delta^{11(12),13(18)}$, 3β-OH, 4α-$CH_2OH$, 17-$CH_2OH$. 3β,23,28-Trihydroxyolean-11,13(18)-diene
143. [46] $\Delta^{11(12),13(18)}$, 3β-OH, 16- =O, 17-$CH_2OH$. 3β,28-Diacetoxyolean-11,13(18)-dien-16-one
144. $\Delta^{11(12),13(18)}$, 3β-OAc, 16- =O, 17-$CH_2OAc$. 3β,28-Diacetoxyolean-11,13(18) dien-16-one
145. [13] $\Delta^{11(12),13(18)}$, 2α-OH, 3α-OH, 4β-$CH_2OH$, 17-COOMe. 2α,3α,24-Trihydroxyolean-11,13(18)-dien-28-oic acid (M.E.)
146. $\Delta^{11(12),13(18)}$, 2α-OAc, 3α-OAc, 4β-$CH_2OAc$, 17-COOMe. 2α,3α,24-Triacetoxyolean-11,13(18)-dien-28-oic acid (M.E.)
147. [44] $\Delta^{9(11),12(13)}$, 3β-OH, 16β-OH, 17-$CH_2OH$. Saikogenin B
148. $\Delta^{9(11),12(13)}$, 3β-OH, 4α-$CH_2OH$, 16β-OH, 17-$CH_2OH$. Saikogenin H
149. [47] $\Delta^{9(11),12(13)}$, 3β-OAc. 3β-Acetoxyolean-9(11),12-diene
150. $\Delta^{9(11),12(13)}$, 3β-OAc, 6β-OH. 3β-OAc. 3β-Acetoxyolean-9(11),12-diene
151. $\Delta^{9(11),12(13)}$, 3β-OAc, 6- =O. 3β-Acetoxyolean-9(11),12-dien-6-one
152. [17] $\Delta^{9(11),12(13)}$, 3- =O. Olean-9(11),12-dien-3-one
153. [49] $\Delta^{18(19)}$, 3- =O. 17-COOMe. Moronic acid (M.E.)
154. $\Delta^{18(19)}$, 3β-OH, 17-COOMe. Morolic acid (M.E.)

155. [50] $\Delta^{18(19)}$, 3β-OH. Germanicol
156. $\Delta^{18(19)}$, 3β-OAc. 3-O-Acetylgermanicol
157. $\Delta^{18(19)}$, 1β-OH, 3β-OH. Anagadiol
158. $\Delta^{18(19)}$, 1β-OH, 3β-OAc. 3-O-Acetylanagadiol
159. $\Delta^{18(19)}$, 3β-OAc, 17-COOH. 3-O-Acetylmorolic acid
160. $\Delta^{18(19)}$, 3β-OAc, 17-$CH_2$OAc, 3,28-Diacetylmoradiol
161. $\Delta^{18(19)}$, 3β-OAc, 17-$CH_2$OH. 3-O-Acetylmoradiol
162. [51] $\Delta^{18(19)}$, 3β-OMe. 3-O-Methylgermanicol
163. [50] $\Delta^{18(19)}$, 3- =0. Germanicone
164. $\Delta^{18(19)}$, 3- =0, 11- =0. Olean-18-ene-3,11-dione
165. $\Delta^{18(19)}$, 3- =0, 16- =0. Olean-18-ene-3,16-dione
166. $\Delta^{18(19)}$, 3β-OH, 11α-OH. Nivadiol
167. $\Delta^{18(19)}$, 3β-OAc, 11α-OAc. 3,11-Di-O-acetoxylnivadiol
168. $\Delta^{18(19)}$, 3β-OH, 11β-OH. Olean-18-ene-3β,11β-diol
169. $\Delta^{18(19)}$, 3β-OAc, 11β-OAc. 3β,11β-Diacetoxyolean-18-ene
170. $\Delta^{18(19),1(2)}$, 3- =0. Olean-1,18-dien-3-one
171. $\Delta^{18(19)}$, 3- =0, 1α-0-2α. 1α,2α-Epoxyolean-18-en-3-one
172. [52] 3β-OAc, 12α-OH, 13β-0-CO-17. 3β-Acetoxy-12α-hydroxyolean-28,13-olide
173. 3β-OH, 13β-0-CO-17. 3β-Acetoxyolean-28,13-olide
174. 3β-OH, 13β-0-CO-17. 3β-Hydroxyolean-28,13-olide
175. [53] 3β-OH, 12- =0, 16β-OH, 20β-CHO, 21β-OCOPh. Avenestergenin B-2
176. 3β-OH, 4α-$CH_2$OH, 12- =0, 16β-OH, 20β-CHO, 21β-OCOPh. Avenestergenin A-2
177. [31] 3β-OH, 13β-$OCH_2$-17, 16α-OH, 20β-CHO, 22β-OAc. Androsacenol
178. [54] 3β-OH, 13β-$OCH_2$-17, 16α-OH, 20β-CHO. Cyclamiretin A
179. [53] 3-=0, 19β-$OCH_2$-17, 18α-H. 19β-28-Epoxy-18α-oleanan-3-one
180. 2α-$CH_3$, 3- =0, 19β-$OCH_2$-17, 18α-H. 2α-Methyl-19β,28-epoxy-18α-oleanan-3-one
181. 2β-$CH_3$, 3- =0, 19β-$OCH_2$-17, 18α-H. 2β-Methyl-19β,28-epoxy-18α-oleanan-3-one
182. 1- =0, 19β-$OCH_2$-17, 18α-H. 19β,28-Epoxy-18α-oleanan-1-one
183. 1- =0, 2α-$CH_3$, 19β-$OCH_2$-17, 18α-H. 2α-Methyl-19β-28-epoxy-18α-oleanan-1-one
184. 1- =0, 2β-$CH_3$, 19β-$OCH_2$-17, 18α-H. 2β-Methyl-19β,28-epoxy-18α-oleanan-1-one
185. 19β-$OCH_2$-17, 18α-H. 19β,28-Epoxy-18α-oleanane
186. 2β-$CH_3$, 19β-$OCH_2$-17, 18α-H. 2β-Methyl-19β,28-epoxy-18α-oleanane
187. 3β-OH, 19β-$OCH_2$-17, 18α-H. 19β,28-Epoxy-18α-oleanan-3β-ol
188. 2α-$CH_3$, 3β-OH, 19β-$OCH_2$-17, 18α-H. 2α-Methyl-19β,28-epoxy-18α-oleanan-3β-ol

## LITERATURE CITED

1. F. W. Wehrli and T. Nishida, Prog. Chem. Org. Nat. Prod., 36, 96 (1979).
2. J. W. Blunt and J. B. Stothers, Org. Magn. Res., 9, 439 (1977).
3. P. K. Agrawal, D. S. Jain, and R. Thakur, Phytochemistry, 24, 2479 (1985).
4. J. N. Shoolery, J. Nat. Prod., 47, 226 (1984).
5. H. Beierbeck, J. K. Saunders, and J. W. ApSimon, Can. J. Chem., 55, 2813 (1977).
6. N. C. Kumar and S. Sabramanian, Modern Techniques in High-Resolution FT NMR, Springer-Verlag, New York (1987), p. 44.
7. A. Inada, M. Yamada, H. Murata, M. Kobayashi, H. Toya, Y. Kato, and T. Nakanishi, Chem. Pharm. Bull., 36, 4269 (1988).
8. U. Kizu and T. Tomimori, Chem. Pharm. Bull., 30, 3340 (1982).
9. T. Takemoto, S. Arihara, K. Yoshikawa, F. Tanaka, and T. Hayashi, Yakugaku Zasshi, 105, 834 (1985).
10. S. R. Johns, J. A. Lamberton, T. C. Morton, H. Suares, and R. I. Willing, Austr. J. Chem., 36, 2537 (1983).
11. R. Pedera-Miranda, G. Delgado, and A. Romo de Vivar, J. Nat. Prod., 49, 225 (1986).
12. A. Ikuta and H. Itokawa, Phytochemistry, 25, 1625 (1986).
13. H. Kojima, H. Tominaga, S. Sato, and H. Ogihara, Phytochemistry, 26, 1107 (1987).
14. T. Takemoto, S. Arihara, K. Uoshikawa, K. Kuzumoto, I. Yano, and T. Hayashi, J. Pharm. Soc. Jpn., 104, 246 (1984).
15. R. Kasai, M. Miyakoshi, R.-N. Nie, J. Zhou, K. Matsumoto, T. Morita, M. Nishi, K. Miyahara, and O. Tanaka, Phytochemistry, 27, 1439 (1988).
16. U. Wrzesiono, L. Zaprulko, J. Budzianowski, N. Wojtowicz, and D. Dubowska, Magn. Res. Chem., 25, 223 (1987).
17. R. A. Barnes, A. L. Periera, T. L. V. Scofild, R. B. Filho, and A. C. Pinto, Chem. Pharm. Bull., 32, 3674 (1984).

18. A. G. Gonzalez, C. M. Gonzalez, A. G. Ravelo, X. A. Dominguez, and B. M. Fraga, J. Nat Prod., 49, 148 (1986).
19. R. Kasai, T. Onaka, G.-R. Yang, J. Zhou, and O. Tanaka, Chem. Pharm. Bull., 39, 1486 (1987).
20. G. S. Ricca, B. Danieli, G. Palmisano, H. Duddeck, and M. H. A. Elgamal, Org. Magn. Res., 11, 163 (1978).
21. H. Duddeck, M. H. A. Elgamal, G. S. Ricca, B. Danieli, and G. Palmisano, Org. Magn. Res., 11, 130 (1978).
22. G. A. Tolstikov, L. M. Khalilov, A. Baltina, R. M. Kondratenko, A. A. Panasenko, and E. V. Vasil'eva, Khim. Prir. Soedin., 645 (1985).
23. A. Bongini, M. Contento, M. Orena, G. P. Pifferi, and R. Erba, Org. Magn. Res., 22, 61 (1984).
24. K. Hidaka, M. Ito, Y. Matsuda, H. Kohda, K. Yamasaki, and J. Yamahara, Phytochem., 26, 2023 (1987).
25. M. Yoshikawa, N. Murakami, T. Tanigama, Y. Hamamoto, T. Nakae, and I. Kitigawa, Tetrahedron Lett., 28, 2029 (1987).
26. A.-A. Damidar, J. Reisch, and M. Amer, Chem. Pharm. Bull., 27, 2938 (1979).
27. T. K. Chen, D. C. Ales, N. C. Baenziger, D. F. Wiemer, J. Org. Chem., 48, 3525 (1983).
28. Guang-Li Yiang, A. I. Gray, and P. G. Waterman, Phytochemistry, 27, 2283 (1988).
29. E. Akai, T. Takeda, Y. Kobayashi, and Y. Ogihara, Chem. Pharm. Bull., 33, 3715 (1985).
30. H. Ishii, K. Tori, T. Tozyo, and Y. Yoshimura, J. Chem. Soc., Perkin Trans. I, 1928 (1981).
31. B. C. Pal, G. Roy, and S. B. Mahato, Phytochemistry, 23, 1475 (1984).
32. A. K. Chakravarty, B. Das, and S. Pakrashi, Phytochemistry, 26, 2345 (1987).
33. T. Takeshita, S. Hamada, and T. Nohara, Chem. Pharm. Bull., 37, 846 (1989).
34. V. Piozzi, M. Paternostro, S. Passannanti, and E. Gacs-Baitz, Phytochemistry, 25, 539 (1986).
35. A. S. R. Anjaneyulu, M. Bapuji, L. R. Row, and S. Sree, Phytochemistry, 18, 463 (1979).
36. J. E. KinJo, I. Miyimoto, K. Murakami, and K. Kida, Chem. Pharm. Bull., 33, 1293 (1985).
37. D. C. Jain, R. S. Thakur, A. Bajpai, and A. R. Sood, Phytochemistry, 27, 1216 (1988).
38. Y. Chen, T. Takeda, and Y. Ogihara, Chem. Pharm. Bull., 33, 127 (1985).
39. T. Konoshima and K.-H. Lee, J. Nat. Prod., 49, 650 (1986).
40. A. S. R. Anjaneyulu and A. V. Prasad, Phytochemistry, 21, 2057 (1982).
41. F. Abe and T. Yamauchi, Chem. Pharm. Bull., 35, 1833 (1987).
42. T. Takemoto, N. Nishimoto, S. Nakai, N. Takagi, S. Hayashi, S. Odashima, and Y. Wada, Tetrahedron Lett., 24, 1057 (1983).
43. Y. Kobayashi, T. Takeda, and Y. Ogihara, Chem. Pharm. Bull., 29, 2222 (1981).
44. K. Shimizu, S. Amagaya, and Y. Ogihara, Chem. Pharm. Bull., 33, 3349 (1985)
45. R. Tschesche, S. Sepulveda, and T. M. Braun, Chem. Ber., 113, 1754 (1980).
46. Y. Kobayashi, M. Ogawa, and Y. Ogihara, J. Chem. Soc., Perkin Trans. I, 2277 (1981).
47. J. G. Diaz, B. M. Fraga, A. G. Gonzalez, P. Gonzalez, M. G. Hernandez, and J. M. Miranda, Phytochemistry, 23, 1474 (1984).
48. H. Eggert and C. Djerassi, J. Org. Chem., 38, 3788 (1973).
49. P. L. Majumder, R. N. Maiti, S. K. Panda, D. Mal, M. S. Raju, and E. Wenkert, J. Org. Chem., 44, 2811 (1979).
50. A. G. Gonzalez, B. M. Braga, P. Gonzalez, M. G. Hernandez, and A. G. Ravelo, Phytochemistry, 20, 1919 (1981).
51. J. W. Blunt and M. H. B. Munro, Org. Magn. Res., 13, 26 (1980).
52. M. Katai, T. Terai, and H. Meguzi, Chem. Pharm. Bull., 31, 1567 (1983).
53. M. J. Begley, L. Crombie, W. M. L. Crombie, and D. A. Witing, J. Chem. Soc., Perkin Trans. I, 1905 (1986).
54. J. P. Waltho, D. H. Williams, S. B. Mahato, B. C. Pal, and J. C. Barna, J. Chem. Soc., Perkin Trans. I, 1527 (1986).
55. B. C. Paul and S. B. Mahato, J. Chem. Soc., Perkin Trans. I, 1963 (1987).
56. M. Budesinsky and J. Klinot, Collect. Czech. Chem. Commun., 54, 1928 (1989).
57. M. I. M. Wazeer, Magn. Res. Chem., 23, 250 (1985).
58. H. Eggert, C. L. Van Antwerp, N. S. Bhacca, and C. Djerassi, J. Org. Chem., 41, 71 (1976).
59. C. L. Van Antwerp, H. Eggert, G. D. Meakins, J. O. Miners, and C. Djerassi, J. Org. Chem., 42, 789 (1977).
60. R. Roques, J. P. Declercq, and G. German, Acta Crystallogr., 34, 2367 (1978).

61. S. Harkar, T. K. Razdan, and E. S. Waight, Phytochemistry, 23, 2893 (1984).
62. C. B. Rogers, Phytochemistry, 27, 3217 (1988).

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# OXIDIZED LIPIDS OF COTTON-PLANT LEAVES

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and A. I. Glushenkova

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Free fatty acids and diacylglycerols containing them have been isolated from the leaves of a cotton plant of a wilt-resistant variety. The composition and structures of the hydroxylipids have been determined by a combination of the methods of IRS, UVS, GLC, and the mass spectrometry of TMS derivatives, and changes in the composition of the hydroxy acids taking place on artificial infection of the plant with the fungus *Verticillium dahliae* Kleb. have been revealed.

On the penetration of a parasitic fungus into plant tissues, lipid peroxide oxidation processes (LOPs) are activated in them [1]. The LOP metabolites include a broad set of oxygenated fatty acids (OFAs), which have been isolated in recent years from the vegetative organs of resistant and susceptible varieties of rice [2], tomatoes [3], and the plant *Phleum pratense* [4]. In the resistance varieties, OFAs are present in healthy tissues, and in the susceptible varieties they are biosynthesized in response to infection stress. The OFAs that have been described possess a pronounced fungitoxicity and are capable in low concentrations of inducing systemic resistance in varieties susceptible to infection.

We have carried out research studies of the OFAs in young healthy leaves of a cotton plant of the resistant variety 175F (sample I) and in leaves of the same plant artificially infected with cotton wilt (sample II).

The surface lipids were first removed from the freshly-gathered leaves. After nonlipid impurities had been eliminated from the cell lipids, these lipids were separated with the aid of CC on silica gel into neutral and polar fractions. The neutral lipids were separated into classes by rechromatography using CC and TLC. According to TLC results in system 1 and qualitative reactions with picric acid and 2,4-dinitrophenylhydrazine, the neutral lipids I and II contained no epoxy or oxo derivatives. The fractions corresponding in their chromatographic mobility to a mixture of 1,2(1,3)-diacylglycerols (DAGs) and hydroxylipids ($R_f$ 0.3) amounted for sample I to 2.1 and for sample II to 2.9 mg/g of dry tissue substance.

To determine the classes of the hydroxylipids, parts of the fractions of samples I and II were converted into trimethylsilyloxy (TMS) derivatives, and these were analyzed by mass spectrometry.

The mass spectra of the TMS derivatives of hydroxylipids I and II had no fundamental qualitative differences. In them the strongest peaks were those of the ion $(M - 31)^+$ with m/z 371-411 formed as the result of the breakdown of the di-TMS ethers of hydroxy acids with the general formula $CH_3(CH_2)_nCHOTMS(CH_2)_mCOOTMS$. The peaks of the $M^+$ ions with m/z 358-470 and the $(M - 15)^+$ ions with m/z 343-455 had low intensities and the mass numbers of these peaks showed that some of the main components of these fractions were free monohydroxy acids with chain lengths of from 12 to 20 carbon atoms and from 0 to 2 double bonds.

Another series of strong peaks included those of $(M - 15)^+$ ions with m/z 625, 651, and 677 and of $(M - 90)^+$ ions with m/z 550, 576, and 602, which were assigned to the main high-mass fragments from the breakdown of the TMS ethers of DAGs [5] of the 16:0–16:0-TMS, 18:1–16:0-TMS, and 18:1–18:1-TMS types. The peaks of $M^+$ (m/z 640, 666, and 692), $(M - 103)^+$ with

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