lowed to stand overnight at room temperature, the reaction mixture was extracted with ether (150 ml.). The ether solution was washed with 5% sodium hydroxide solution and with water, and then was dried and evaporated. The residue was fractionated, giving the product, b.p. 160°/0.2 mm., yield 5.1 g. (73%).

The aryl alkyl thionocarbonates described in Table II could be prepared by either of these procedures, except that when the alcohol was *n*-heptyl or higher, better results were obtained when the reaction was performed in the presence of pyridine.

Thiolcarbonates: S-Allyl *p*-Tolyl Thiolcarbonate.—A solution of *p*-tolyl chlorothionoformate (15.0 g., 0.081 mole) in allyl alcohol (15 g.) was refluxed for 2 hr. The solution was evaporated and the residue was fractionated, giving the product, b.p. 136–138°/10 mm., yield 13.2 g. (78%).

All of the thiolcarbonates listed in Table III could be prepared in this way.

S-(1-Methylallyl) *p*-Tolyl Thiolcarbonate.—*p*-Tolyl chlorothionoformate (12.1 g., 0.065 mole) was added to a solution of 2-buten-1-ol (14.0 g., 0.19 mole) in pyridine (20 ml.) at 10° over a period of 25 min. After being allowed to stand for 3 hr., the reaction mixture was diluted with ether (200 ml.). The ether solution was washed with 5% sodium hydroxide solution and with water, and was then evaporated at room temperature under reduced pressure to constant weight (5.65 g., yield 39%). A portion of the product was distilled (b.p. 107–108°/0.7 mm.) for analysis. Both the distilled and the undistilled fractions were analytically pure, and both had infrared spectra identical with that of the product prepared as described above.

S-(2-Chloroethyl) 3,4-dichlorophenyl thiolcarbonate was prepared by this procedure.

Hydrolysis of S-(2-Chloroethyl) 3,4-Dichlorophenyl Thiolcarbonate.—A suspension of the thiolcarbonate (14.25 g., 0.05 mole) in 1 *N* potassium hydroxide solution (150 ml.) was allowed to stand for 18 hr. The suspension was acidified and extracted with ether (3 × 100 ml.), and the ether extract was evaporated to dryness. Fractionation of the residue yielded 3,4-dichlorophenol, b.p. 98–100°/0.8 mm., yield 8.10 g. (99%). The product melted at 65–66° after recrystallization from petroleum ether (60–90°), and did not depress the melting point of a known sample.

Hydrolysis of S-(1-Methylallyl) 2-Chloro-4-nitrophenyl Thiolcarbonate.—A solution of the thiolcarbonate (0.485 g., 0.00169 mole) in 1 *N* aqueous potassium hydroxide (5.5 ml.) and methanol (15 ml.) was allowed to stand overnight. The solution was acidified and extracted with ether (3 × 50 ml.), and the ether extract was dried and evaporated. The residue was dried at 70°/20 mm., giving 2-chloro-4-nitrophenol, m.p. 107–109°, yield 0.259 g. (89%). There was no depression on admixture with a known sample.

The Nuclear Magnetic Resonance Spectra of Pentacyclic Triterpenes[1,2]

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Received July 6, 1962

The n.m.r. spectra of a series of pentacyclic triterpenoidal derivatives have been studied, and some correlations between structures and spectra have been made.

The present study of the n.m.r. spectra of pentacyclic triterpenes was initiated with the hope that the spectra obtained would help in the structural elucidation of new pentacyclic triterpenes, and perhaps assist in establishing the class to which a triterpene of unknown structure belongs.

The n.m.r. spectra of a series of pentacyclic triterpenes were studied using tetrachloroethylene as the solvent and chloroform (10%) as an internal standard. In order to have uniform and dependable results, the same amount of triterpene was almost always used (20 mg.), but in a few cases less than this quantity was employed because of a limited supply of the pure compound. The spectra were recorded at 40 megacycles/second with a Varian Associates High Resolution Nuclear Magnetic Resonance spectrometer equipped with a Varian Associates super-stabilizer. All absorptions were calibrated by the audiofrequency side band technique. *Values given for the chemical shifts are in parts per million, with tetramethylsilane taken as zero and chloroform as 7.25.*

In an effort to increase the solubility of the triterpenes and make the spectra more significant, most of the triterpenes were converted to their corresponding methyl ester acetate derivatives. Since the ursane, oleanane, and lupane series are the most widespread of the pentacyclic triterpenes found in nature, the majority of the triterpenes studied here belong to these three groups. A few triterpenes of unknown or of recently elucidated structure were included in the study. On p. 4513 are given the structures and conformations of α-amyrin (I and Ia), β-amyrin (II and IIa), and lupeol (III and IIIa), the simplest alcohols of the ursane, oleanane, and lupane series respectively.

Discussion

Some Characteristics of the N.m.r. Spectra of Pentacyclic Triterpenes.—Many distinct absorptions can be found in the spectra of pentacyclic triterpenes. Methyl esters and acetoxyl groups give sharp absorptions.[5] Angular methyl groups also give well defined absorptions. However, since pentacyclic triterpenes contain a number of

(1) Parts of this paper appeared as a preliminary communication in *Chem. Ind.* (London), 1092 (1959).

(2) This research was supported in part by Grant RG-5442 from the National Institutes of Health.

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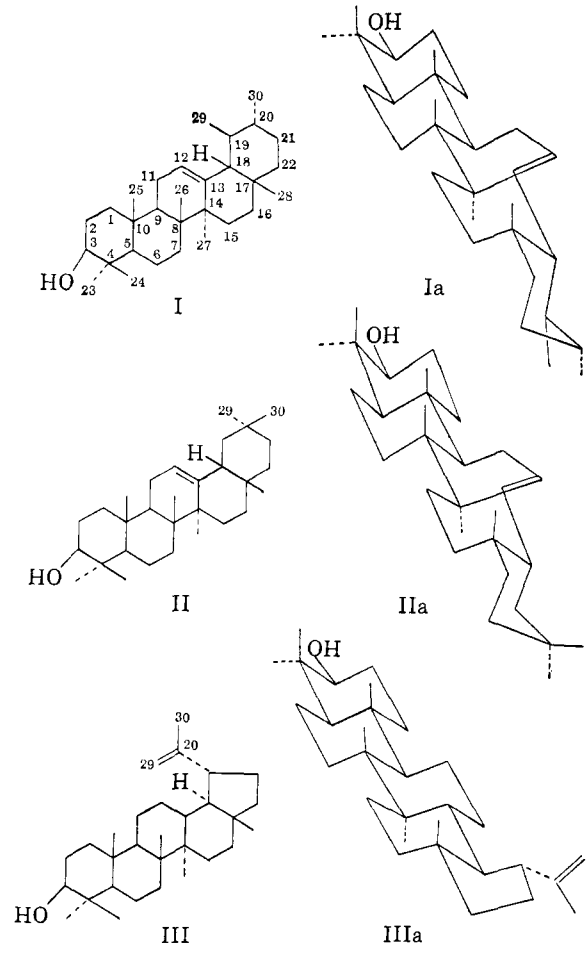
(5) R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *J. Am. Chem. Soc.*, **80**, 6098 (1958).



such methyl groups their absorptions often are found to overlap.

Certain other functional groups such as vinylic protons, protons alpha to hydroxyls or acetoxyls, and methylene protons, all were found to have low and diffuse absorptions. Even so, these absorptions are important because they give a clue to certain structural features of the triterpenes.

In Fig. 1A is given a typical spectrum of a pentacyclic triterpenoidal derivative, namely ursolic acid methyl ester acetate. The vinylic proton, being the least shielded in the molecule, is found to give a broad absorption (11 c.p.s.) with a peak at 5.11. An even broader absorption is that of the proton alpha to the acetoxyl group centered at 4.41 and 23 c.p.s. broad.[6] This last absorption sometimes is hard to locate since it is quite weak, but nevertheless it has been found that it can yield information on the nature of the acetoxyl group. Both the carbomethoxyl and the acetoxyl protons give sharp singlet absorptions, at 1.955 and 3.533, respectively. The methylene absorptions may be found very poorly defined between 1.25 and 2.00. The sharp peaks at the right end of the spectrum represent the highly shielded angular methyl groups. Although ursolic acid contains seven

(6) J. N. Shoolery and Max T. Rogers, *J. Am. Chem. Soc.*, **80**, 5121 (1958).

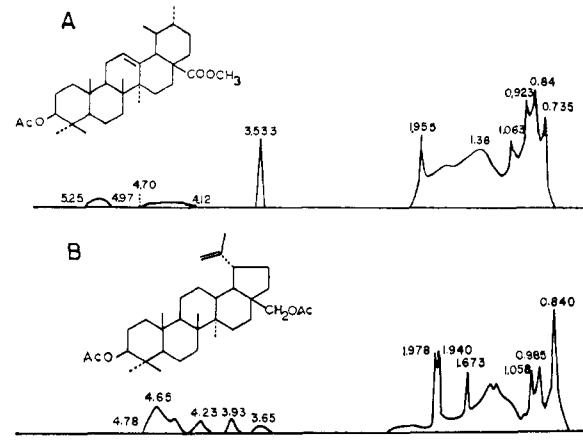


Fig. 1.—Nuclear magnetic resonance spectra of: A, ursolic acid methyl ester acetate; B, betulin diacetate, taken in tetrachloroethylene solution, with chloroform as internal standard, at 40 Mc./sec.

methyl groups, only four distinct peaks are visible, indicating a large amount of overlapping.

In Table I, placed under the respective groups to which they belong, are listed the various triterpenoids studied. Four belong to the ursane series, seventeen belong to the oleanane series, and four to the lupane series. One triterpene, namely friedelin, was studied which has been clearly recognized to involve a nuclear structure other than the three previously mentioned.

Chemical Shift of the Highest C-Methyl Group.—Whenever a carbomethoxyl function is present in the molecule, it was noticed that the chemical shift of the highest (most shielded) C-methyl group is partially indicative of the position of the carbomethoxyl. Thus, *in every case in which a C-28 carbomethoxyl function is present in a triterpene of the ursane or oleanane series, the highest C-methyl absorption peak appears upfield from 0.775.* Alternatively, when the C-28 position is represented either by a hydroxymethylene, a methyl group, or a lactone, the highest C-methyl absorption peak appears downfield from 0.775.

A few of the triterpenoids were found to have their highest C-methyl absorption close to the dividing line; however, most were far to one side or the other. Even compounds of the lupane group seemed to obey this empirical rule. For example, lupanol and betulin diacetate (Fig. 1B) were found to have their highest absorptions at 0.803 and 0.840, respectively, while melaleucic acid methyl ester which is known to possess a C-28 carbomethoxyl function exhibits a methyl absorption at 0.695. Furthermore, morolic acid methyl ester acetate (Fig. 2A), which has a C-28 carbomethoxyl group and a double bond at 17(18) rather than at the usual 12(13) position, has a spectrum which also conforms with the rule. Friedelin is the only naturally occurring triterpene which has its highest C-methyl absorption below 0.775 and which did not possess a C-28 carbomethoxyl function.

TABLE I
TRITERPENOIDS STUDIED

Ursane Group
α-Amyrin benzoate
Uvaol diacetate
Ursolic acid methyl ester acetate
Asiatic acid methyl ester triacetate

Oleanane Group
β-Amyrin benzoate
Erythrodiol diacetate
Longispinogenin triacetate
Soyasapogenol-B triacetate
Chichipegenin tetraacetate
A_1-Barrigenol pentaacetate
7β-Hydroxy-A_1-barrigenol hexaacetate (phillysapogenol hexaacetate)
11-Keto-A_1-barrigenol pentaacetate
Dumortierigenin diacetate
Oleanolic acid methyl ester acetate
Cochalic acid methyl ester
Arjunolic acid methyl ester triacetate
Echinocystic acid methyl ester diacetate
α-Boswellic acid methyl ester acetate
11-Keto-α-boswellic acid methyl ester acetate
Glycyrrhetic acid methyl ester acetate
Morolic acid methyl ester acetate

Lupane Group
Lupanol
Betulin diacetate
Melaleucic acid methyl ester
Thurberogenin acetate

Other Triterpenes
Friedelin
Phillyrigenin diacetate

It must be remembered, however, that this triterpene has a radically different nuclear structure, so that one would not expect it to conform to this generalization. It will be noticed that a number of the triterpenes studied possessed carbomethoxyl groups at other than the C-28 position, and again all of these had their highest methyl absorptions downfield from 0.775.

Two of the triterpenes studied, namely, thurberogenin acetate and dumortierigenin diacetate (Fig. 2B), had a lactone ring involving a C-28 carbonyl function. In both of these cases the highest C-methyl peak was downfield from 0.775 so that even these compounds comply with the rule since they do not incorporate a carbomethoxyl group at C-28.

One has to use some discretion when using the conclusions reached above. The value of 0.775 has been set empirically. It could be made a little smaller or larger and the rule would still hold. Not all known pentacyclic triterpenes have been investigated, so that exceptions might be found. As mentioned above, only one compound containing a double bond at other than the usual C-12(13) position in the oleanane series has been studied, so that extrapolation of this rule to all triterpenes should be avoided.

The basic reason behind this empirical rule is not clear. It may be due to the bulky carbomethoxyl group causing some strain in the mole-

TABLE II
CHEMICAL SHIFTS OF HIGHEST C-METHYL GROUPS

Triterpenes	Chemical shifts	C-28 Carbomethoxyl functions
Arjunolic acid methyl ester triacetate	0.683	Yes
Melaleucic acid methyl ester	.695	Yes
Echinocystic acid methyl ester diacetate	.713	Yes
Oleanolic acid methyl ester acetate	.715	Yes
Oleanolic acid methyl ester	.730	Yes
Ursolic acid methyl ester acetate	.735	Yes
Cochalic acid methyl ester	.735	Yes
Asiatic acid methyl ester triacetate	.763	Yes
Morolic acid methyl ester acetate	.765	Yes
A_1-Barrigenol pentaacetate	.783	No
α-Boswellic acid methyl ester acetate	.788	No
Glycyrrhetic acid methyl ester acetate	.808	No
Soyasapogenol-B triacetate	.808	No
7β-Hydroxy-A_1-barrigenol hexaacetate	.820	No
Uvaol diacetate	.823	No
Longispinogenin triacetate	.825	No
Chichipegenin tetraacetate	.845	No
α-Amyrin benzoate	.865	No
Erythrodiol diacetate	.875	No
β-Amyrin benzoate	.905	No
11-Keto-α-boswellic acid methyl ester acetate	.848	No
Lupanol	.803	No
Betulin diacetate	.840	No
Friedelin	.703	No
Thurberogenin acetate	.810	No
Dumortierigenin diacetate	.860	No

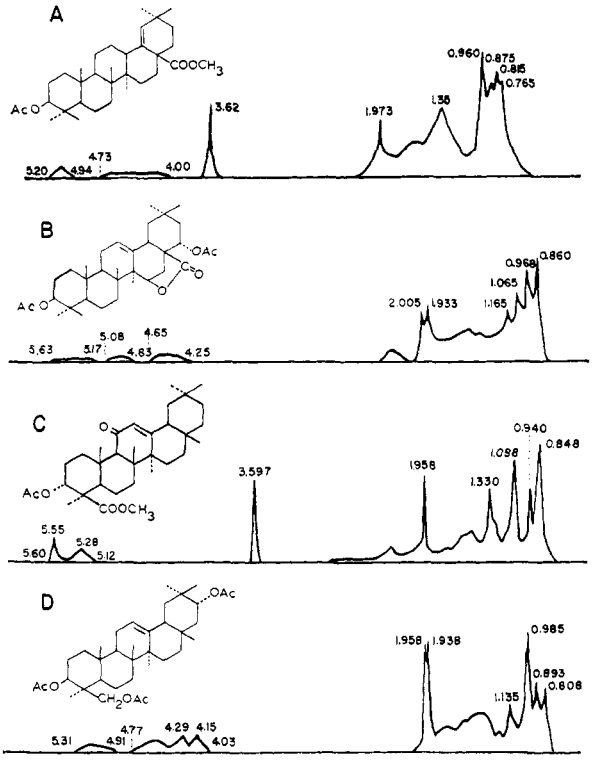


Fig. 2.—Nuclear magnetic resonance spectra of: A, morolic acid methyl ester acetate; B, dumortierigenin diacetate; C, 11-keto-α-boswellic acid methyl ester acetate; D, soyasapogenol-B triacetate, taken in tetrachloroethylene solution, with chloroform as internal standard, at 40 Mc./sec.

cule; or possibly the magnetic anisotropy of this group might result in increased shielding of an angular methyl group.

Methyl Ester Absorption.—The position of the absorption of the methoxyl moiety of a methyl ester is also partially indicative of the relative position of the carbomethoxyl group in the triterpene molecule. Thus, *the absorption of a C-28 methyl ester belonging to the oleanane or ursane group is usually upfield from 3.595 while the carbomethoxyls located in other positions such as at C-24 or at C-30 absorb further downfield in the region from 3.595 to 3.650.*

Therefore, there are two ways to verify the presence of a C-28 carbomethoxyl group in an ursane or oleanane triterpene, namely, from the chemical shift of the highest angular methyl, and from the position of the methoxyl group absorption. Thirteen esters were studied and eleven of these belonged to the oleanane and ursane series and had a normal double bond at C-12(13). All were found to obey the ester rule mentioned above (see Table III).

TABLE III
ABSORPTION OF METHYL ESTERS

Triterpenes	Methoxyl absorptions	Position of carbomethoxyl function
Ursolic acid methyl ester	3.578	C-28
Asiatic acid methyl ester triacetate	3.538	C-28
Ursolic acid methyl ester acetate	3.535	C-28
Arjunolic acid methyl ester triacetate	3.538	C-28
Oleanolic acid methyl ester acetate	3.555	C-28
Cochalic acid methyl ester	3.570	C-28
Oleanolic acid methyl ester	3.580	C-28
Echinocystic acid methyl ester	3.595	C-28
11-Keto-α-boswellic acid methyl ester acetate	3.597	C-24
Melaleucic acid methyl ester	3.608	C-28
Morolic acid methyl ester acetate	3.618	C-28
α-Boswellic acid methyl ester acetate	3.640	C-24
Glycyrrhetic acid methyl ester	3.645	C-30

Since several methyl esters have their absorptions very close to the dividing line, 3.595, the distinction between the two classes of esters is not so clear as when the chemical shift of the highest C-methyl group is considered. Two methyl esters can be considered as special and anomalous cases, namely, the pair derived from melaleucic acid and morolic acid. Melaleucic acid belongs to the lupane series, while morolic acid as mentioned previously is an oleanane type triterpene with its double bond at C-17(18).

As in the case of the C-methyl absorption, the reason for the differences in the positions of the methyl ester absorptions is not known. It may be related to the fact that the C-28 carbomethoxyl function is extremely hindered, or that this functional group is influenced by the magnetic anisotropy of the 12(13) double bond.

Vinyl Proton Absorption.—*The proton of the normal trisubstituted double bond in the ursane and oleanane series absorbs in the region between 4.93 and 5.50.* This absorption is broad and its center is poorly defined. However, if the double bond is conjugated with a carbonyl function at C-11, such as in 11-keto-α-boswellic acid methyl ester acetate (Fig. 2C), the vinylic proton is found to absorb at lower field, *i.e.*, at 5.55, and the peak becomes much sharper (6 c.p.s. broad). This downfield shift is to be expected since the keto group is electron withdrawing and causes the vinyl proton to be less shielded, while the sharpening of the peak can be easily explained by the absence of any alpha hydrogens.

If a terminal double bond is present, such as in the lupane series, the vinyl protons absorb at higher field, i.e., around 4.30 to 5.87. This type of vinylic absorption is easily recognized by its larger size since it represents two protons. Morolic acid methyl ester acetate (Fig. 2A), which has a C-17(18) double bond, shows a well defined vinylic absorption for a trisubstituted double bond at 5.07 (10 c.p.s. broad).

The above conclusions were put to practical use in the course of the structural elucidation of the pentacyclic triterpene 7β-hydroxy-A$_1$-barrigenol.[7,8] This compound was known to contain six hydroxyl groups and to be related probably to A$_1$-barrigenol. The nuclear magnetic resonance spectrum of 7β-hydroxy-A$_1$-barrigenol hexaacetate seemed to indicate that a normal trisubstituted double bond was present; but the vinylic peak overlapped with other protonic absorptions. To get around this overlapping of absorptions, the spectrum of the diethylidene diacetate derivative of 7β-hydroxy-A$_1$-barrigenol was obtained. This spectrum clearly exhibited a vinylic peak at 5.26 (10 c.p.s. broad) with no interference from other functional groups, thus indicating the presence of the usual 12(13) double bond.

Vinylic Methyl Absorption.—Another useful and characteristic absorption was found to be that of the vinylic methyl function, CH$_3$—C=C. Normal methyl groups absorb from 0.625 to 1.500. *Vinylic methyl peaks usually appear between 1.63 and 1.80, and are sharp and well defined.* Although this absorption is in the methylene region, vinylic methyl peaks stand out enough to be clearly identified. Many triterpenes of the lupane class have vinylic methyl groups whose absorption can be recognized easily. Thus, betulin diacetate, melaleucic acid methyl ester, and thurberogenin acetate exhibited vinylic methyl peaks at 1.67, 1.64, and 1.80, respectively.

(7) J. O. Knight and D. E. White, *Tetrahedron Letters*, **3**, 100 (1961).

(8) The authors also received a sample of R$_1$-barrigenol hexaacetate from Prof. Yau Tang Lin, Department of Chemistry, National Taiwan University, Taipei, Taiwan. Both the n.m.r. and infrared spectra of this compound and of 7β-hydroxy-A$_1$-barrigenol hexaacetate obtained through Dr. J. O. Knight, Department of Chemistry, University of Western Australia, Nedlands, Western Australia, proved to be identical.

Acetoxyl Absorption.—Acetoxyl protons give the sharpest absorption of any function in the triterpene series. This absorption usually appears between 1.82 and 2.07, with the majority of such protons absorbing between 1.92 and 1.97. Since acetoxyl peaks are sharp and clear, a difference of even 0.02 p.p.m. between two peaks can still be recognized. There does not seem to be any distinguishable difference between the acetates of primary and secondary alcohols.

In Lemieux's study on the nuclear magnetic resonance spectra of cyclic polyol acetates,[5] it was found that axial acetoxyl groups absorb at lower field than the corresponding equatorial substituents. In the present study, three triterpene derivatives studied possessed axial acetoxyl functions, namely, α-boswellic acid methyl ester acetate and its 11-keto derivative (Fig. 2C), and echinocystic acid methyl ester diacetate. The spectra of the first and third of these compounds exhibited acetoxyl peaks at 1.993 and 2.073, respectively. These values are low compared to most acetoxyls, which absorb above 1.97. On the other hand, 11-keto-α-boswellic acid methyl ester acetate had its acetate absorption at 1.958. Therefore, nuclear magnetic resonance spectroscopy cannot clearly differentiate between axial and equatorial acetoxyl functions in the triterpene series if only the acetoxyl absorption is considered. Soyasapogenol-B triacetate (Fig. 2D), a triterpene of as yet partially unknown structure, had its lowest acetate peak at 1.958, but no really safe conclusion regarding the position and stereochemistry of the third acetoxy group in this triterpenoid derivative can be derived at this time.

The acetoxyl groups of 1,2-glycols, as in the acetates of arjunolic acid, asiatic acid (Fig. 3A), A_1-barrigenol, and 7β-hydroxy-A_1-barrigenol, always appeared as twin peaks separated by a few cycles. Furthermore, such functions absorbed at higher fields (1.85 to 1.92) than acetoxyl groups of analogous monoacetates. This phenomenon may provide an easy method for the characterization of vicinal gycols. It must be pointed out, however, that in the present study triterpenes containing only *trans* diequatorial 1,2-glycols were studied.

The spectrum of 7β-hydroxy-A_1-barrigenol hexaacetate is particularly interesting because it has an acetoxyl peak absorbing at 2.220 although as mentioned previously, the usual acetoxyl absorption is between 1.92 to 1.97. This anomalous absorption probably is due to the 7β-acetoxyl function. This acetate group is sterically hindered and in the immediate vicinity of the C-15 acetate.

Protons Alpha to Secondary Acetoxyl Groups.—The absorption of protons alpha to acetoxyl groups usually appears as a broad hump. This type of absorption may be grouped into two classes depending on whether the acetoxyl group is primary or secondary.

A proton alpha to a secondary acetoxyl group gives an absorption which is about 30 c.p.s. broad. However, this peak is so low in intensity that unless a concentrated solution is used the signal may be obscured by the noise. Since the present study used only small quantities of triterpenes, it was a major problem to locate this absorption with any degree of accuracy.

It was found that the axial C-3 proton of an acetylated triterpene absorbs between 4.00 to 4.75. The corresponding equatorial proton, as in α-boswellic acid methyl ester acetate or its 11-keto derivative, absorbs some twenty-nine cycles beyond the axial at 5.00 to 5.48 and does not exhibit as broad an absorption as the axial proton. Shoolery and Rogers[6] noted this same effect in the steroids, namely, that the equatorial protons showed up at lower fields than the axial. In the present study, however, it was found that there is a specific exception to this generalization. If a strong 1,3-interaction is present between an axial proton and an angular methyl group, that axial proton will absorb at lower field.[9] Thus, the axial proton at C-16 in longispinogenin triacetate (Fig. 3B) absorbs relatively downfield and is centered at 5.62 (22 c.p.s. broad) because of interaction with the C-27 methyl group. Again, in chichipegenin tetraacetate, which has three protons alpha to secondary alcohol acetates, only one of these three protons can be clearly distinguished, with its absorption centered at 5.81 (25 c.p.s. broad). By analogy with longispinogenin triacetate, this low absorption must again be due to the sterically hindered C-16 proton.

Dumortierigenin diacetate has two axial protons alpha to acetoxyl groups at C-3 and C-22, and an equatorial proton at C-15 alpha to the lactone ring oxygen. The spectrum (Fig. 2B) of this compound shows one absorption centered at 5.44 (18 c.p.s. broad) representing one proton, and another absorption centered at 4.45 (16 c.p.s. broad) representing two protons. Hence the former absorption represents the C-15 equatorial proton, while the latter is due to the two axial protons.

If one considers Spring's structure for soyasapogenol-B triacetate[10] (Fig. 2D) to be correct (namely 3β,21α,24-trihydroxyolean-12-ene triacetate), there should be present two protons alpha to secondary acetoxyl functions located at C-3 and C-21 respectively. In the latter position, the alpha proton would be equatorial and would be expected to absorb at low field. However, both alpha protons are found to absorb upfield from 4.75.

Protons Alpha to Acetylated 1,2-Glycols.—Triterpenes often contain 1,2-glycol functions and most frequently these are found at C-2, C-3, and at C-15, C-16. It was found that the *protons alpha*

(9) S. Brownstein, *J. Am. Chem. Soc.*, **81**, 1606 (1959).
(10) H. M. Smith, J. M. Smith, and F. S. Spring, *Tetrahedron*, **4**, 111, 1958.

to an acetylated 1,2-glycol appear at much lower field than the protons alpha to isolated acetoxyl groups, and give sharper peaks, with areas indicating two protons. In the present study four triterpenes were studied containing acetylated *trans* diequatorial vicinal glycol systems, and the absorptions are recorded in Table IV.

TABLE IV

ABSORPTIONS OF PROTONS ALPHA TO ACETOXYL GROUPS IN ACETYLATED 1,2-GLYCOLS

Triterpenes	Widths of absorptions	Peaks	Positions of acetoxyl groups
Arjunolic acid methyl ester triacetate	4.70–5.18[a]	4.98	2, 3
Asiatic acid methyl ester triacetate	4.70–5.18[a]	5.00	2, 3
A_1-Barrigenol pentaacetate	5.23–5.69[b]	5.54	15, 16
7β-Hydroxy-A_1-barrigenol hexaacetate	5.25–5.64[a]	5.36	15, 16

[a] 19 c.p.s. [b] 16 c.p.s.

A possible reason for the paramagnetic shift in the absorption of the C-15 and C-16 protons is that they exhibit 1,3 diaxial interactions with the C-26 and C-27 methyl functions respectively.

Protons Alpha to Primary Acetoxyl Functions.—The methylene protons of an acetoxymethyl group may absorb as a sharply defined singlet, as in longispinogenin triacetate (Fig. 3B), or doublet as in soyasapogenol-B triacetate (Fig. 2D), or quartet as in erythrodiol diacetate (Fig. 3C), probably depending upon the degree of steric hindrance. *The position of the absorption was found to vary over a wide range depending on the relative position of the methylene group in question.* Table V lists the triterpenoids containing acetoxymethyl functions and the corresponding absorptions. Hence nuclear magnetic resonance spectroscopy can be of definite use in establishing the position of acetoxymethyl groups. Before these results were obtained, the position of the acetoxymethyl group in asiatic acid had not been definitely settled. The present work strongly indicated that this group was at C-23.[11] Another interesting case is that of phillyrigenin diacetate (Fig. 3D),[12] a triterpenoid of still unknown structure, but known to possess a hydroxymethylene group. The nuclear magnetic resonance spectrum of phillyrigenin diacetate showed a peak at 4.26 due to the methylene protons of the acetoxymethyl group. Hence by analogy with soyasapogenol-B triacetate, the primary alcohol is probably at C-24.

TABLE V

ABSORPTIONS OF METHYLENE PROTONS OF ACETOXYMETHYL GROUPS

Triterpenes	Absorptions	Types[a]	Positions
Arjunolic acid methyl ester triacetate	3.65	s.	23
Asiatic acid methyl ester triacetate	3.65	s.	23
A_1-Barrigenol pentaacetate	3.82	q.	28
11-Keto-A_1-barrigenol pentaacetate	3.85	q.	28
Uvaol diacetate	3.88	q.	28
Erythrodiol diacetate	3.85	q.	28
Phillysapogenol hexaacetate	3.89	q.	28
Longispinogenin triacetate	4.00	s.	28
Betulin diacetate	4.05	q.	28
Soyasapogenol-B triacetate	4.22	d.	24
Phillyrigenin diacetate	4.26	s.	(24)
A_1-Barrigenol pentaacetate	5.08	d.	27
7β-Hydroxy-A_1-barrigenol hexaacetate	5.18	s.	27
11-Keto-A_1-barrigenol pentaacetate	5.20	d.	27

[a] s. = singlet, d. = doublet, and q. = quartet. A doublet is actually a quartet type splitting with two extra absorptions caused by an almost forbidden transition and, therefore, giving too weak a signal to be picked up.

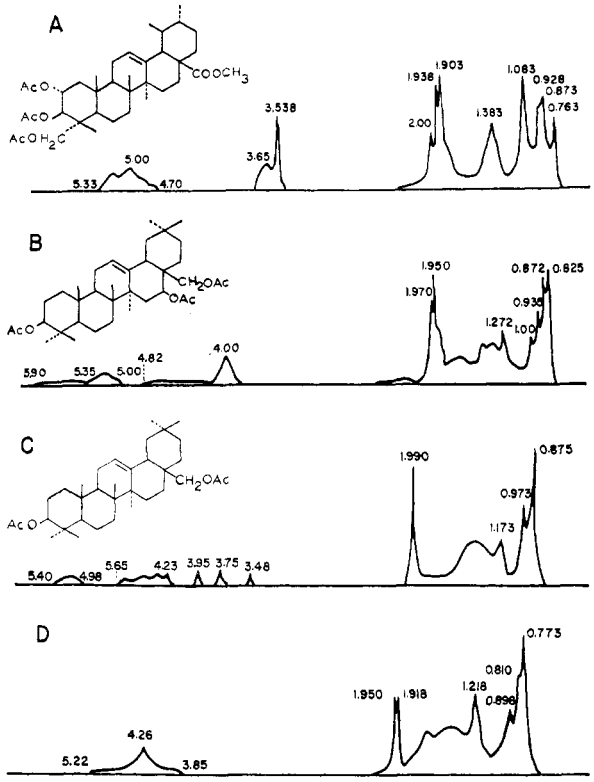


Fig. 3.—Nuclear magnetic resonance spectra of: A, asiatic acid methyl ester triacetate; B, longispinogenin triacetate; C, erythrodiol diacetate; D, phillyrigenin diacetate, taken in tetrachloroethylene solution, with chloroform as internal standard, at 40 Mc./sec.

Acknowledgment.—Most of the triterpenes in this study were very kindly supplied by Professors C. Djerassi, J. Polonsky, L. Fieser, E. J. Corey, T. J. King, M. O. Farooq, Yau-Tang Lin, and Drs. O. Knight and A. Sosa. This study would not have been possible without their assistance and cooperation.

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